BENEFICIATION OF ULTRAFINE HIGH SULPHUR COAL

Final Report

by

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ABSTRACT

The pyrite particles in Prince Mine coal which was used in our experiments were found to be characterized by a bimodal distribution: the coarse mode is between about 20 and 40 μm and the fine mode is less than about 15 μm with a modal size of 4 μm. All forms of pyrite are predominantly associated with vitrinite. Only very long wet grinding, in our test for 50 minutes, which provides the product characterized by median size of 10.44 μm allows sufficient (but not complete) pyrite liberation.

Separation of the pyrite from coal by means of the oil agglomeration and the dissolved-air flotation was not satisfactory. Otisca T agglomeration process, in which Freon 113 is utilized instead of oily hydrocarbons, did not provide sufficient selectivity either.

Neither two-stage reverse flotation, nor the use of frothers only were successful. Only the use of carboxymethyl cellulose (CMC) as modifying agent under alkaline conditions, with kerosene as a collector and some MIBC allow high grade clean coal concentrates (less than 0.5% pyritic sulphur from coal containing about 2.6% pyritic sulphur) to be obtained at good recoveries (about 75%). A key to a high selectivity under such conditions is a few cleaning stages.

Because of a bimodal pyrite particles size distribution, in the rational flowsheet the coarse pyrite grains should be removed by gravity methods (tabling, water-only hydrocyclones, etc.) and only then followed by a very fine grinding of the precleaned coal and the flotation.

INTRODUCTION

One of the main reasons to clean coal is removal of the pyritic sulphur. The separation of pyrite from coal is very efficient in gravity separation methods which are based on the differences in coal and pyrite densities. Although the gravity methods are excellent for removal of coarse pyrite, separation efficiency decays drastically with the size of the particles. Effective pyrite liberation usually necessitates fine grinding, and as a result, flotation is a main fine coal cleaning process. It should, however, be noted that whereas the conventional frots flotation is efficient as a means of removing the ash-forming material, the principal defect with the process is its inefficiency in removing pyrite. Thus, our ability to separate pyrite and coal to a large extent depends on the pyrite mineralization; if it is finely disseminated and then needs fine grinding for liberation, the subsequent desulphurization by flotation is not very selective. Therefore, most of the recent research effort over the past decade has been in the area of sulphur removal by flotation. A useful review of our state-of-art in this area was recently published by Miller and Deurbrouck.[1]

Coal flotation is based on the differences in surface properties of hydrophobic coal particles and hydrophilic inorganic gangue. The floatability of coal-pyrite is somewhat different than that of ore-pyrite.[2,3] Among various options, the two-stage reverse flotation with the depression of coal with dextrin in the second stage seems to be the most studied. This process is based on the selective adsorption of dextrin on hydro-

phobic particles through hydrophobic interactions.[4,5] Another possibility offers the use of carboxymethyl cellulose, the reagent tested extensively in the selective flocculation of coal slimes,[6,7] and in the coal flotation.[8] Our recent studies on the adsorption of carboxymethyl cellulose on a model solid, graphite, revealed that it interacts with hydrophobic solids through inorganic impurities (Ca, Fe) which serve as adsorption centres.[9] Therefore, while CMC adsorption on the graphite purified by leaching is very low and does not cause any significant depression, the floatability of natural graphite samples is strongly depressed with CMC.

Humic acid seems to offer another possibility in the selective flotation of coals.[8,10]

Oil agglomeration, which is a likely alternative to coal flotation in cleaning fine coal, is unable to separate selectively pyrite from coal. Wheelock et al.[11] tested pretreatment in 2% Na_2CO_3 solutions at 50-80°C before oil agglomeration to enhance the selectivity of the pyrite removal. They also showed that the selectivity of oil agglomeration is improved at alkaline pH's.

In the 1970's, Krukiewicz and Laskowski[12] described the magnetizing alkali leaching process. They showed that the magnetic susceptibility of siderite particles may be increased by pretreatment in alkaline solutions which facilitates subsequent magnetic separation of siderite ores. The same concept has been further tested by Hall and Finch[13] who have shown that similar pretreatment also improves magnetic separation of pyrite from coal.

During the last three years, CANMET has sponsored a research pro-

gram at the University of British Columbia in which the use of various modifying agents in the desulphurizing flotation of coal has been studied. This year the research program has been divided into four major groups:

(a) Studies on the pyrite liberation during fine grinding of high sulphur coal from Nova Scotia.

(b) Exploratory tests on the separation of fine coal and pyrite using the Dissolved-Air Flotation (DAF) process.

(c) Exploratory tests on the separation of fine coal and pyrite in oil agglomeration. The Otisca T process has also been tested.

(d) Bench-scale froth flotation tests of the finely ground high-sulphur coal with the use of various modifying agents.

MATERIALS AND METHODS

Two samples of the high-sulphur coal from Nova Scotia have been used in the experiments: the sample referred to as a DEVCO coal supplied by CANMET (described in last year's report[8]), and a new sample (Sample 2) supplied directly by Prince Mines, Sydney, Nova Scotia.

Most flotation experiments were carried out with Sample 2.

Proximate Analysis (Sample 2)

Moisture	1.64%
$Volatiles_{(dry)}$	28.1 %
$Ash_{(dry)}$	13.2 %
Fixed $Carbon_{(dry)}$	58.7 %
$Volatiles_{(dmmf)}$	32.37%
Fixed $Carbon_{(dmmf)}$	67.62%
Pyritic Sulphur	2.76%
Total Sulphur	3.7 %

Sample 1 was used only in the experiments on Dissolved-Air Flotation (DAF).

The preparation of Sample 2 for flotation experiments is depicted in Figure 1. As seen, wet grinding in the laboratory rod mill for 21 min.

provides material 90% below 38 μm (400 mesh).

The effect of longer grinding times on the particle size distribution (determined with Elzone Apparatus) is shown in Figure 2.

Mean content of pyritic sulphur in the raw coal (Sample 2) calculated from the data in Figure 1 is below 3%, while the total sulphur content is in the range from 3.6 to 3.8%.

Pyritic sulphur was determined according to Standard ASTM procedures. The samples were first extracted with dilute hydrochloric acid, water-washed, and the pyrite was leached from the insoluble residue (remaining after the HCl treatment) with dilute nitric acid. The iron extracted into this portion of the solution was determined by atomic adsorption and the pyritic sulphur was calculated as a stoichiometric combination with the iron.

The Eschka analytical procedure was used to determine the total sulphur of the coal.

PYRITE OCCURRENCE AND LIBERATION*

Methods

All coal samples were formed into pellets using a transoptic powder and polished using standard procedures with the final grit size of 0.05 μm. The samples were then examined using an image analysis (Leitz Tass ®) to determine the size distribution of the pyrite. About 1,000 pyrite particles were measured per sample and population parameters determined. For description purposes, the coal was also examined using standard coal petrographic techniques.

Mode of Occurrence of Pyrite

Six uncrushed coal samples were exposed to evaluate the initial size distribution of the pyrite. The results of these analyses (Figure 3) indicate the raw coal has a bimodal distribution and that there is considerable variation from sample to sample. The coarse mode of pyrite consists of massive sub-hedral to anhedral forms with a modal diameter of 30 μm. The fine fraction includes two different pyrite forms:

(1) framboidal pyrite that ranges from 5 to 10 μm in diameter, and

(2) fine single particles of pyrite that range in size from less than 1 μm to 5 μm in diameter.

All forms of pyrite are predominantly (est. greater than 95%) associated with and are intergrown in the various forms of vitrinite. In some vitri-

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*Authored by Dr. Marc Bustin

nite particles, pyrite infills cell lumens but in most grains the pyrite is randomly distributed. Pyrite is rarely associated with liptinite, inertinite or semi-inertine macerals.

Variations in Size Distribution of Pyrite and Degree of Liberation With Grinding

The relative abundance of pyrite, and the size distribution of pyrite in various samples are shown in Figures 4 to 8. From examination of the samples and the analysis, some general observations are noteworthy (refer to Plate 1).

1. The pyrite in all samples not crushed below 53 μm has bimodal distribution. The coarse mode is between about 20 and 40 μm and the fine mode is less than about 15 μm with a modal size of 4 μm.

2. Samples crushed below 53 μm for the most part have a unimodal distribution with a mode between 3 and 7 μm. The pyrite is poorly sorted.

3. The amount of liberated pyrite increases with increased time of grinding. The coarse pyrite fraction is liberated more readily (less grinding) than fine pyrite. Even prolonged grinding however (50 min.) does not liberate the finest pyrite particles (less than 2 μm).

4. Wet grinding of samples is more efficient at liberation of

pyrite than dry grinding.

5. The size distribution of pyrite and the coal particles shows a progressive and predictable shift with increased grinding (Plate 1 and Figure 2).

DISSOLVED-AIR FLOTATION TESTS*

The dissolved-air flotation (DAF) setup used in our experiments (Figure 10) comprises:

(a) Source of compressed air;

(b) Glass flowmeter;

(c) Saturator;

(d) Pressure reduction device;

(e) Flotation cell;

(f) Water level control in cell.

The unit can be used in batch and continuous tests. The procedure involves coal pulp conditioning with desired reagents, followed by mixing with the supersaturated water (SSW) carrying the microbubbles. The floated product is then scraped off at the top every few minutes. As water is being introduced into the flotation cell, there is a continuous flow of pulp (referred to as "underflow") out of the cell. Mass and water balances can be constructed by collecting all products after the test.

Experimental Procedure

Batch tests

a) A 250 g sample of DEVCO coal (Sample 1) is ground with 750 ml of water in the rod mill for 25 min. to obtain 97.6%

*Experiments carried out by Dr. Jaime Solari

minus 38 μm. (After 35 min. of grinding, 99% of the mill products is finer than 38 μm.)

b) Coal slurry is carefully stirred and split for various tests.

c) Three pressure reduction devices with 0.34, 0.5 or 1.0 mm diameter orifice plates were available. These devices will give SSW flowrates (Q_S) of about 130, 290 and 950 ml/min. respectively at a saturator injection pressure of 60 psig. Note that the choice of orifice will determine the flotation time.

d) Next the pressure reduction device is to be carefully connected with the inlet tube of the cell, the bleed-off valve on top of the saturator is removed and the saturator is filled with water. The saturation capacity is 7 litres, but because the injection valve is 1 litre above the bottom of the device, only about 6 litres of SSW are available for use in the DAF test. Reagents MIBC, NaOH may be added into saturator.

e) The main pressure valve is open when the pressure is about 5 psig higher than the saturation pressure (P_S), and then 5 l/min. of air is allowed into the saturator at the required P_S. For P_S > 40 psig., about 20 min. is sufficient to achieve equilibrium concentration of air dissolved in water.

f) The coal pulp is then added into the flotation cell and some more water (≈ 5.5 litres) is added. The stirrer (Canlab), set at level 4, is used to condition at required pH and with

depressants (CMC, $KMnO_4$, etc.) for 8 mins.

g) Collector (kerosene) is emulsified with MIBC in 250 ml of water in the Waring Blender for 1 min. and is introduced into the cell with stirrer set at level 5; followed by 2 min. more conditioning. Then the stirring is reduced to level 0.

h) More water is added into the cell up to 6 l. mark. The initial recycle ratio (R_i) is defined as the ratio of the volume of SSW added to fill up the cell to the volume of feed ($R_i = V_s/V_f$). The cell volume (V_c) is 7 l. so that in this case $R_i = 0.167$. Obviously, tests can also be carried out with $R_i = 0$.

i) The pulp level in the cell must be maintained a few millimetres below the upper cell level with the water control device (WLC). The SSW injection valve (time zero) is then opened and the time taken to fill up cell is recorded. When cell is filled, the underflow valve is turned on and the position of WLC (if necessary) is corrected so that only the scraped concentrate froth overflows into the launder.

j) Concentrate is collected into trays. When using high SSW flowrates, e.g. with the 1.0 mm orifice, the flotation is to be stopped to take the concentrate sample. In this case, the injection valve is shut down and the sample is collected with the stirrer put off. When ready to continue, the stirrer is switched on and after 30 seconds the valve is open with time

set to zero again. Usually three samples are taken, and four with the other pressure reduction devices.

k) When the test is completed, the volume of pulp underflow (V_{uv}) is measured and filtered. Tailings are collected also. With these data, metallurgical, water and mass balances are carried out as follows:

Mass Balance:

$$C_1 + C_2 + \ldots + C_m + \text{Mass of cell tails} + \text{Mass of underflow tailings} = \text{Feed Mass}$$

where C_i is mass of concentrate i.

Water Balance:

$$Q_s \cdot t_f = (V_c - V_F) + V_{UF} + V_{conc.}$$

where $V_{conc.}$ is water reporting to the concentrate and t_f is total flotation time. Note that water recovery = $V_{conc.}/Q_s \cdot t_f$.

Metallurgical Balance:

$$\text{(Sulphur)} \quad S_F \cdot F = \sum_{i=1}^{m} S_i \cdot C_i + S_T \cdot T + S_{UV} \cdot UV$$

$$\text{(Ash)} \quad \alpha \cdot F = \sum_{i}^{m} \lambda_i \cdot C_i + \lambda_T \cdot T + \lambda_{UV} \cdot UV$$

where F, i, T and UV refer to feed, concentrate i, cell and underflow tailings respectively. S and λ stand for sulphur and ash analysis (%) in each product; α is the mean ash content in the raw coal.

Results

Results of the experiments are shown in Figures 11 to 18. As already pointed out, the choice of the orifice (pressure reduction device) changes the flowrate of the supersaturated water and then affects the flotation rate.

Results for the orifice of 1 mm in diameter are given in Figure 11 and for the orifice of 0.34 mm in diameter in Figure 12. Comparison of the flotation kinetics at the same concentration of kerosene (7.1 ± 0.6 kg/t) for three orifices are shown in Figure 13.

Figure 15 shows the yield of concentrates and the total sulphur content in concentrates as a function of kerosene addition at two pH levels: 5.2 and 10.2. As seen, selectivity is much better under alkaline conditions. Figure 16 further confirms such conclusions.

Dissolved-air flotation is very different from conventional froth flotation. Froth product is skimmed from the surface and there is no thick froth layer. This seems to result from the very limited amount of air in the cell which is continuously released from inflowing supersaturated water. As this inflow is limited, the amount of air in the cell is limited too. Figure 17 shows that the selectivity and the yield of concentrate do not depend on the concentration of MIBC in the broad range studied. This further confirms the different mechanism from the conventional froth flotation.

As seen from Figure 18, sulphur content in concentrate is not correlated with water in froth product, but is correlated with ash content. It confirms that despite all obvious differences from froth flotation, it is still a flotation process.

Probably the most important conclusion concerns the amount of reagents which are required. These amounts are much higher than that in froth flotation. It seems that selective aggregation of fine particles is a prerequisite to the successful dissolved-air flotation. In spite of very high reagent consumptions, the process is quite sensitive to the pH. To check such a conclusion, we have constructed a small DAF setup and tested flotation of narrow size fractions of Fording metallurgical coal in 10^{-3}M solutions of MIBC. The results showed that only particles larger than 25 μm floated under such conditions. Dissolved-air flotation does not then seem to be a solution for flotation of very fine particles.

The main deficiency with the process is that microbubbles are released from the injected supersaturated water and this limits seriously air hold-up in the cell and in consequence the throughput of the device. Pressurization of the flotation pulp seems to be an obvious solution which should be further studied.

OIL AGGLOMERATION

Both oil agglomeration and coal flotation rely on differences in the surface properties of hydrophobic coal and hydrophilic inorganic gangue. Oil agglomeration has also been shown to be able to treat selectively very fine feeds.[14] Even better selectivity has been claimed in the Otisca T process which utilized Freon 113 instead of oil.[15]

In our tests with the use of Freon 113, 50 g of the coal (Sample 2) ground for 21 minutes was agglomerated in 500 ml of water with the addition of varying amounts of Freon (from 16 to 32%). Agglomeration experiments were carried out in a high speed cocktail mixer and the agglomerated product was recovered by passing over 30 mesh screen. The results are given in Table 1. Recovery has been in the over-80% range, but the selectivity (1.8 - 2% S_{FeS_2}) was not very promising.

The process was also conducted in the lab mill as practised by the Otisca T process. In this experiment, 500 g of coal was ground in 1 litre of water in the presence of 100 ml of Freon 113 for 21 minutes, followed by separation on the screen. The recovery of combustible was excellent, over 90%, but again the selectivity was inferior to those obtained with the use of conventional mixing devices.

These exploratory tests confirmed good recoveries but at this point, the selectivity in our flotation studies was already substantially better and so it has been decided to concentrate our efforts on further improvement of the flotation procedures.

Table 1

Oil Agglomeration with the Use of Freon 113

No.	Freon 113 (ml)	% Solid	Cond. Time (min)	Weight (gm)	% Ash	S_{FeS_2}	Yield (%)	Recovery of Combustible Matter (%)
11	10	10	5	C 39.52 T 8.80	7.41 36.06	2.07 6.2	81.79	86.67
12	8	10	5	C 37.11 T 11.05	8.51 27.85	1.84 5.17	77.06	80.98
13	14	10	5	C 42.07 T 5.46	6.24 59.81	1.84 7.92	88.51	94.73
14	10	10	10	C 29.38 T 18.76	8.67 19.46	2.3 4,02	61.03	63.98
15	10	10	3	C 40.19 T 9.15	6.94 40.46	1.84 6.55	81.46	87.29
22	10	10	7	C 42.07 T 6.68	6.57 46.86	1.95 6.77	86.30	91.72
23	10	14	5	C 41.05 T 7.53	8.46 33.51	1.95 5.4	84.50	88.24
24	10	7	5	C 40.17 T 8.39	5.96 42.33	1.84 6.31	82.72	88.65
21*	100 ml/ 500 g	13	21	C435.9 T 55.88	7.62 52.23	2.65 3.9	88.64	93.78

*oil agglomeration simultaneously with grinding in rod mill.

BENCH FLOTATION EXPERIMENTS

Prince Mine high-sulphur coal (Sample 2) was used in the batch flotation experiments. Denver lab cell modified by Roberts et al.[16] was utilized. The main portion of the flotation experiments was conducted with the feed ground in the rod mill for 21 min. Such a grinding product contains about 90% of the material below 38 μm (400 mesh). The results of last year's experiments seemed to indicate that pyrite liberation at this fineness of ground coal is sufficiently high.

The concentrates obtained with the use of MIBC, and with MIBC in the presence of CMC contained more than two percent of pyritic sulphur. Neither the use of CMC nor the change of pH improved flotation selectivity. Frothing in the presence of MIBC seems to be excessive and this must have created unselective flotation conditions.

The experiments with kerosene carried out in the way outlined in Figure 19 are much more selective. As seen from Figures 20, 21 and 22, the flotation in this case is sensitive to the amount of CMC and the pH. Flotation and selectivity are both enhanced by higher pH (about 9) and this is in line with the previous findings.[8]

The use of humic acid in the tests performed in the manner described previously[8] also confirmed the previous results. In the presence of humic acid flotation selectivity increases after the second addition of the collector and frother; this increase in selectivity is accompanied by a drastic increase in yield of the froth product (Figure 23).

The experiments so far described were carried out simultaneously

with microscopic tests on the pyrite occurrence and liberation and at that point we learned that the grinding of Sample 2 for 21 min. may not be adequate for achieving high degrees of pyrite liberation (approximately 40% of pyrite was found to be not liberated). We then also learned that the pyrite particle size distribution is bimodal and that in the rational flowsheet, the coarser pyrite grains should be removed by gravity methods and only then followed by fine grinding of the precleaned coal and the flotation. It also appeared that further improvement in selectivity might only be achieved by a few stages of cleaning flotation.

The results given in Table 2 pertain to the experiments performed with the use of frothers only. Experiment 114 was conducted on the feed ground for 21 minutes and then floated with 500 g/t MIBC in rougher flotation and an additional 100 g/t MIBC in cleaning. Experiment 115 was run with the use of isopropanol which turned out to be more selective indeed, but at lower concentrate yields.

Experiment 114 with MIBC was repeated with the feed ground for 50 minutes (Experiment 123). The amount of MIBC was to be increased for this experiment (800 g/t MIBC total in rougher flotation with the use of an additional 100 g/t of more selective isopropanol in cleaning). The sulphur content in concentrates was found to be higher than for 21 min. grinding.

The results of this table seem to confirm that MIBC is a very energetic frother which provides high recoveries and that isopropanol, as claimed by some authors,[17] is more selective in coal flotation. In order to achieve comparative yields of the froth products, the addition

Table 2

Results of Flotation Experiments with the Use of Frothers Only

No.	Products	Yield, Wt %	Ash, %	S_{FeS_2}	ΣS_{FeS_2}	S_{FeS_2} Distribution
114	C1	26.7	4.33	0.8	0.8	7.4
	C2	43.2	4.92	1.4	1.16	20.8
	C3	18.6	10.48	3.56	1.66	23.1
	ST	6.5	74.11	11.80		26.7
	PT	5.0	75.70	12.60		22.0
123	C1	48.9	6.23	1.38	1.38	24.8
	C2	25.2	5.45	1.15	1.30	10.6
	C3	12.6	9.33	2.3	1.45	10.6
	ST	9.8	52.70	10.22		36.8
	PT	3.6	71.08	12.97		17.1
115	C1	13.1	5.01	0.9	0.9	4.2
	C2	11.0	4.75	1.03	0.97	4.0
	C3	17.7	4.83	1.03	0.99	6.4
	ST	43.2	12.19	2.65		40.4
	PT	15.0	42.95	8.5		45.0
120	C1	50.6	10.97	2.07	2.07	45.3
	C2	21.4	7.59	1.38	1.89	11.0
	C3	15.7	9.75	2.40	1.97	14.1
	PT	6.3	70.50	10.8		29.5

114 — 21 min grinding; 300 g/t MIBC, 200 g/t MIBC, 3 min rougher flotation; and 2 x 50 g/t MIBC in cleaning; pH natural (≈5.5).

123 — 50 min grinding; 500 g/t MIBC, 300 g/t MIBC; 100 g/t isopropanol in cleaning.

115 — As Exp. 114 but isopropanol was used instead of MIBC. 300 + 200 + 200 + 200 + 200 g/t isopropanol in 10 min rougher flotation; 2 x 100 g/t in cleaning for 6 min; pH natural.

120 — 21 min grinding; salt flotation in 0.6N KCl solution without any other reagents. 3 min rougher flotation without cleaning.

Note: ST = Secondary Tailings
PT = Primary Tailings.

of isopropanol must however by much higher than MIBC (compare Exps. 114 and 115, Table 2). It seems then advisable to use isopropanol instead of MIBC in the cleaning flotations. However, after 50 minutes of grinding even such a combination of reagents did not provide satisfactory results (Experiment 123).

Table 2 also includes the experiment on so-called salt flotation of Prince Mine coal. This experiment was carried out in 0.6 N KCl solution without any other organic reagents.[18] The flotation under such conditions was rapid, selectivity was not satisfactory but we have not studied this process further and have not tried cleanings.

The flotation with the use of kerosene and CMC turned out to be amenable to cleaning. As seen from Table 3, two cleaning stages improve flotation selectivity also after 21 min. grinding (Exps. 65 and 86). It was found then that the flotation carried out with the feed ground 40 or 50 minutes requires doubled amounts of reagents. As seen from the same table, (Experiment 108), the flotation conducted with the feed ground 40 min. is not more selective than after 21 min. grinding (Experiment 65). However, cleaning changes this situation quite clearly. The same is observed with Experiment 106 made after 50 min. grinding; flotation cleaning improves these results further and reduces the pyritic sulphur content in the first concentrate down to about half percent. The use of coal pre-cleaned by tabling allows us to obtain the concentrate at about 75% yield, containing about 0.5% S_{FeS_2} and below 1.75% total sulphur. A complete information on this test is outlined in Figure 24. These promising results are worth further pilot plant tests.

The selectivity in the flotation experiments with CMC and kerosene and its change with grinding is clearly seen from Figure 25.

Carboxymethyl celluloses are manufactured under various trade names. Depramin C (ENKA Industrial Colloids), one of such products, was used instead of CMC in Experiment 118 and these results are also included in the table.

The results of Experiment 122, also included in Table 3, were obtained in the flotation test without CMC. As seen, the pyritic sulphur content in the froth product is very high in this case and this again proves the beneficial effect of CMC as modifier in such a desulphurizing flotation process.

Referring to Table 3 we see that the flotation of precleaned coal by tabling with the use of Humic Acid (Experiment 111) produced quite promising results, too.

All our experiments on the two-stage reverse flotation, which utilizes dextrin in the second stage, have been unsatisfactory and are not discussed in the report.

Table 3

Results of Flotation Experiments with the Use of CMC, Kerosene, and MIBC

No.	Products	Yield, Wt %	Ash, %	S_{FeS_2}	ΣS_{FeS_2}	S_{FeS_2} Distribution
65	Conc. 1	30.0	7.9	1.5	1.5	16.8
	Conc. 2	57.4	7.0	2.07	1.87	44.3
	Tails.	12.6	47.7	8.27	2.68	38.9
86	Clean. 1	32.4	4.53	1.15	1.15	14.1
	Clean. 2	49.7	5.48	1.61	1.43	30.2
	ST	11.4	31.75	6.9	2.09	29.7
	PT	6.5	74.8	10.6	2.65	25.9
88	Clean. 1	81.1	6.72	1.5	1.5	48.3
	ST	11.8	30.1	6.2	2.1	26.8
	PT	6.3	77.7	10.8	2.65	24.9
108	Conc. 1	31.2	8.8	1.61	1.6	19.5
	Conc. 2	60.4	9.9	1.95	1.83	46.6
	Tails.	8.4	60.8	10.10		33.6
109	Clean. 1	25.6	4.8	0.67	0.67	6.9
	Clean. 2	57.8	5.7	1.26	1.08	29.2
	Clean. 3	5.2	24.5	5.75	1.35	12.0
	ST	4.6	78.0	11.6		21.4
	PT	6.9	67.7	11.0		30.6
106	Conc. 1	9.3	8.4	1.5	1.5	5.6
	Conc. 2	58.6	8.2	1.5	1.5	35.3
	Conc. 3	18.5	9.0	1.95	1.6	14.5
	Tails.	13.5	42.9	8.27		44.8
107	Clean. 1	12.4	3.7	0.57	0.57	2.7
	Clean. 2	67.1	4.5	1.03	0.96	26.7
	Clean. 3	6.9	15.35	4.02	0.97	10.7
	ST	4.7	75.5	12.51		22.7
	PT	8.9	56.7	10.8		37.1
122	Clean. 1	45.4	5.78	1.38	1.58	22.3
	Clean. 2	46.0	9.35	2.41	1.90	39.4
	ST	3.5	80.42	12.86		16.0
	PT	5.0	73.62	12.51		22.3

Table 3 (continued)

No.	Products	Yield, Wt %	Ash, %	S_{FeS_2}	ΣS_{FeS_2}	S_{FeS_2} Distribution	
118	Clean. 1	27.4	5.07	0.8	0.80	8.5	
	Clean. 2	57.5	5.82	1.1	1.00	28.3	
	Clean. 3	2.1	18.16	1.2	1.01	3.9	
	ST	6.0	67.69			28.2	
	PT	7.0	64.43			31.0	
110	Clean. 1	30.9	2.22	0.46	0.46	10.5	S_T = 1.65
	Clean. 2	43.0	2.50	0.57	0.52	18.1	S_T = 1.8
	Clean. 3	18.0	5.2	1.84	0.78	24.5	S_T = 2.7
	ST	3.9	47.7	8.38		24.2	S_T = 8.6
	PT	4.1	45.2	7.46		22.6	S_T = 8.26
111	Conc. 1	6.4	8.41	2.2	2.2	10.0	
	Clean. 2	19.3	2.89	0.70	1.07	9.5	
	Clean. 3	17.6	3.18	0.80	0.96	10.1	
	Clean. 4	15.8	3.49	0.92	0.95	10.4	
	ST	38.9	7.73	1.84		51.3	
	PT	2.1	42.04	5.74		8.6	

65 21 min grinding; 100 g/t CMC; 900 g/t kerosene + 100 g/t MIBC; 300 g/t kerosene + 100 g/t MIBC; pH 8.8.

86 As Exp. 65 but with two additonal cleaning flotations; pH 8.9.

88 As Exp. 65, followed by regrinding the froth product with 100 g/t CMC for 10 min and cleaning flotation with additional 300 g/t kerosene + 100 g/t MIBC.

108 40 min grinding; 200 g/t CMC; 1800 g/t kerosene + 200 g/t MIBC; 600 g/t kerosene + 200 g/t MIBC; pH 9.1.

109 As Exp. 108 but with three additional cleaning flotations with 200 g/t MIBC in the second cleaning; pH 8.9.

106 50 min grinding; 200 g/t CMC; 1800 g/t kerosene + 200 g/t MIBC; 600 g/t kerosene + 200 g/t MIBC; pH 9.1.

107 As Exp. 106 but with three additional cleaning flotations with 200 g/t MIBC in the second cleaning; pH 8.8.

122 As Exp. 106, but without CMC.

Table 3 (continued)

118	As Exp. 107, but 200 g/t Depramin was used instead of CMC.
110	As Exp. 107, but with the use of coal precleaned by tabling; 40 min grinding; pH 9 (See flowsheet Figure 24).
111	As Exp. 110, but 2.5 kg/t Humic Acid was used instead of CMC.

CONCLUSIONS

1. Because of a bimodal pyrite particle size distribution, crushing of Prince Mine coal below 0.5 mm allows one-third on the pyrite it contains to be liberated and this portion can be removed from coal by gravity methods (tabling, water-only hydrocyclones, etc.). The other part, finer that 15 μm with a modal size of 4 μm, has not been completely liberated in our tests, even after 50 minutes of wet grinding in the rod mill.

2. Neither the oil agglomeration (Otisca T Process), nor the dissolved-air flotation gave satisfactory results.

3. The use of dextrin in the two-stage reverse flotation did not provide satisfactory results.

4. Flotation tests with the use of frothers only (MIBC, isopropanol) were not successful either. Isopropanol was proved to be a more selective frother than MIBC, but its use is not sufficient to obtain acceptable coal recovery. It seems to be advisable, then, to use isopropanol in cleaning stages.

5. Good selectivity was observed in the direct flotation of coal with kerosene and MIBC in the presence of carboxymethyl cellulose as a modifying agent under alkaline conditions (pH about 9). High grade of concentrates (0.5% pyritic sulphur) can only be obtained after few cleaning stages.

6. Humic Acid used instead of CMC in the flotation with kerosene and

MIBC, used in the way described previously, provided good selectivity which confirms our previous findings.

7. Based on the results of our experimental work, two flowsheets have been designed (Figure 26) and these should further be tested under pilot plant conditions.

ACKNOWLEDGEMENTS

The technical assistance of Kim Peters and Carole Kilshaw, summer assistants, and the Department of Mining and Mineral Process Engineering's Technical Staff members, Sally Finora, Jeff Austin and Peter Kempe, is gratefully acknowledged.

REFERENCES

1. K.J. Miller and A.W. Deurbrouck, Froth Flotation to Desulfurize Coal, in Physical Cleaning of Coal, (Y.A. Liu, Ed.), Marcel Dekker Inc., New York, 1982, pp. 255-291.

2. S.R. Taylor, K.J. Miller and A.W. Deurbrouck, Surface Chemical Problems in Coal Flotation, in Chemistry and Physics of Coal Utilization - 1980, (B.R. Cooper and L. Petrakis, Eds.), Am. Inst. Physics, New York, 1981, pp. 344-356.

3. J.D. Miller, C.L. Lin and S.S. Chang, Coadsorption Phenomena in the Separation of Pyrite from Coal by Reverse Flotation, Coal Preparation International Journal, 1, 1984, 21.

4. J.D. Miller, J. Laskowski and S.S. Chang, Dextrin Adsorption by Oxidized Coal, Colloids and Surfaces, 8, 1983, 137.

5. J. Laskowski and J.D. Miller, New Reagents in Coal Flotation, in Reagents in the Minerals Industry, (M.J. Jones and R. Oblatt, Eds.), Inst. Min. Met., London, 1984, pp. 145-154.

6. Z. Blaschke, Beneficiation of Coal Fines by Selective Flotation, 7th International Coal Preparation Congress, Sydney, 1976, paper F-2.

7. R. Hucko, Beneficiation of Coal Fines by Selective Flocculation, A Laboratory Study. US Bureau of Mines Rep. Invest. No. 8234, Washington, D.C., 1978.

8. J. Laskowski, Comparison of Humic Acid, Dextrin and Carboxymethyl Cellulose as Modifying Reagents in Coal and Coal Pyrite Flotations. DSS Contract OSU83-00103.

9. J.A. Solari, A.C. Araujo and J. Laskowski, The Effect of Carboxymethyl Cellulose on the Flotation and Surface Properties of Graphite, 114th Annual AIME Meeting, New York, February 1985.

10. J. Laskowski, K.S. Moon and L.L. Sirois, Effect of Humic Acid on Floatability of Hydrophobic Solids such as Coals, Proc. 3rd Annual Coal-Liquid Mixtures Workshop, Halifax, October 1983, pp. I-23 to I-43.

11. W.G. Leonard, R.T. Geer, R. Markuszewski and T.D. Wheelock, Coal Desulfurization and Desliming by Oil Agglomeration. Sep. Sci., 16, 1981, 1589.

12. R. Krukiewicz and J. Laskowski, Development of a Magnetizing Alkali Leaching Process for Concentration of Siderite Ores, Proc. 10th Int. Mineral Processing Congress, Inst. Min. Met., London, 1974, pp. 391-410.

13. S.T. Hall and J.A. Finch, Enhanced Magnetic Desulphurization of Coal, Minerals and Metallurgical Processing, Vol. 1, 1984, No. 3, 179.

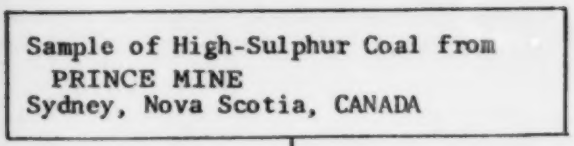
14. C.E. Capes, R.D. Coleman, W.L. Thayer and M. Nakamura, Agglomerative Coal Cleaning for Coal Liquid Mixtures, Proc. 3rd Annual Coal-Liquid Mixtures Workshop, Halifax, October 1983, pp. I-5 to I-20.

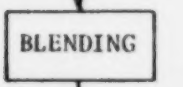
15. D.V. Keller, The Separation of Mineral Matter from Pittsburgh Coal by Wet Milling, in Chemistry of Mineral Matter and Ash in Coal, Am. Chem. Society - Div. Fuel Chemistry, Vol. 29, No. 4, pp. 326-336, 1984.

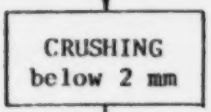
16. T. Roberts, B.A. Firth and S.K. Nicol, A Modified Laboratory Cell for the Flotation of Coal, Int. J. Mineral Processing, 9, 1982, 191.

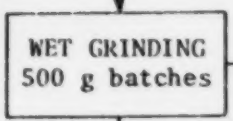
17. J.B. Evans, K. Sury, R.O. McElroy and J. Leja, Agglomeration of Ultrafine Coal Flotation Concentrate: The ACOP Project. To be presented at International Agglomeration Conference, Toronto, June 1985.

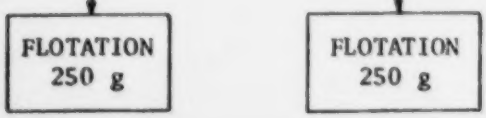
18. J. Laskowski, Flotation of Inherently Hydrophobic Solids in Inorganic Electrolyte Solutions, Proc. Silesian University of Technology, Mining, No. 16, 1966. In Polish.











GRINDING

Time	Size	Yield Wt. %	Ash	S_{FeS_2}	S_{TOTAL}
15 min	+400 mesh	22.6	9.10	1.95	3.00
	-400 mesh	75.7	15.3	3.1	3.84
21 min	+400 mesh	13.5	10.1	1.95	2.89
	-400 mesh	87.1	14.1	3.1	3.87
27 min	+400 mesh	4.8	10.8	2.2	3.14
	-400 mesh	96.2	13.9	3.1	3.84

Figure 1. - Coal Preparation Procedure for Flotation Experiments

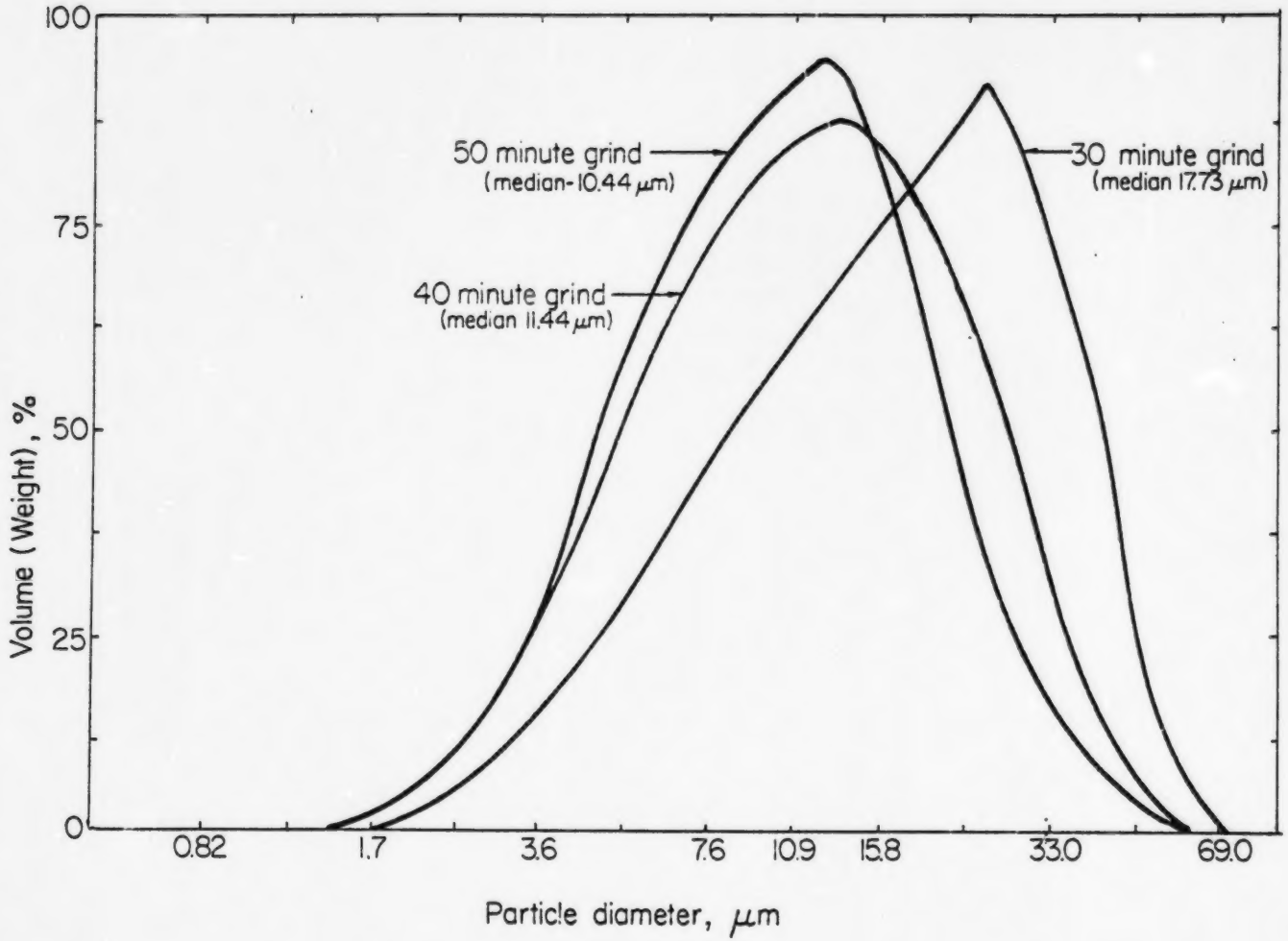


Fig. 2 Particle size distributions of coal sample 2 showing variation with grinding time

Fig. 3 Pyrite particle size distributions on three specimens of sample 2 coal.

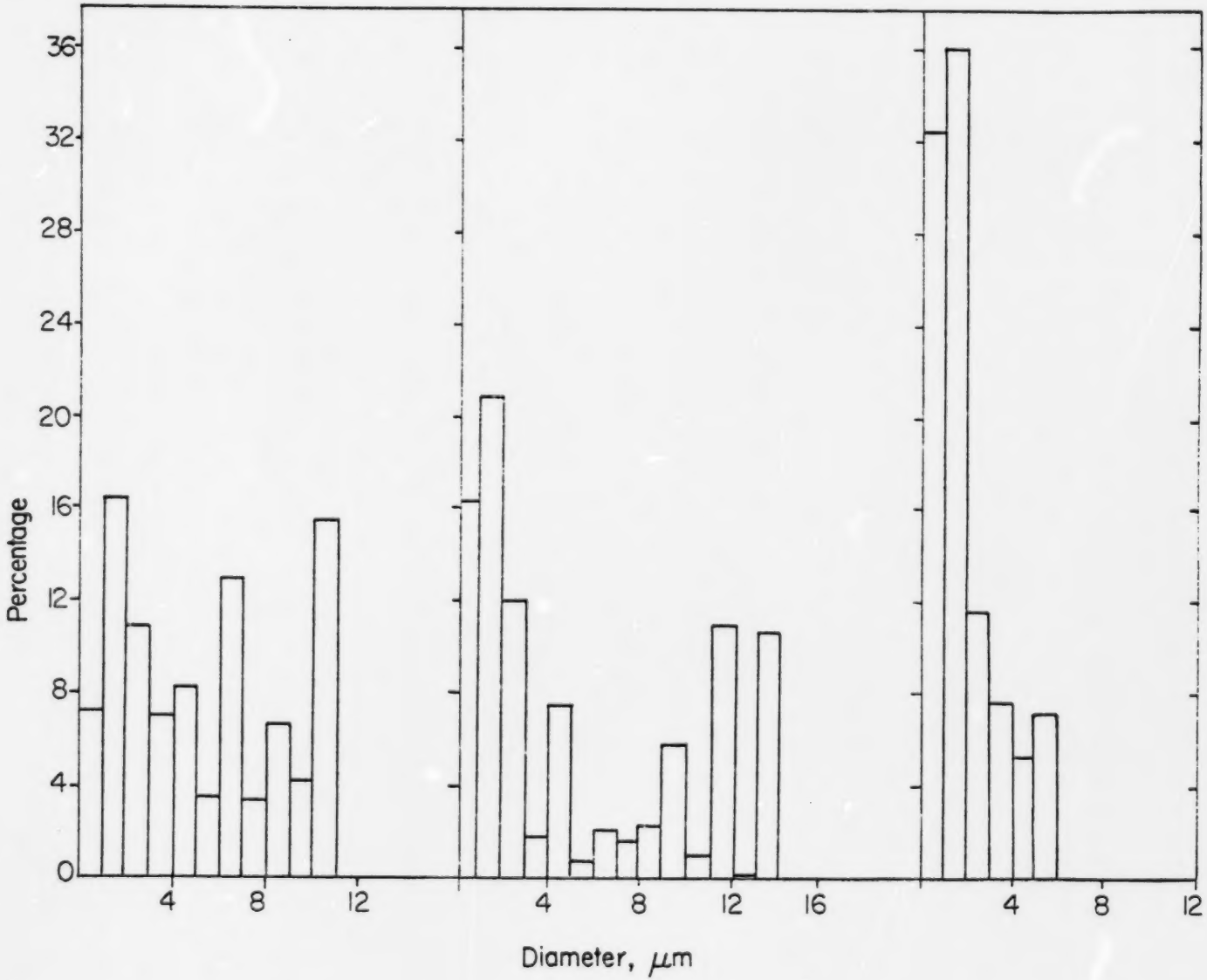


Fig. 4 Pyrite particle size distributions for sample I dry ground below 500 μm and screened into various size fractions

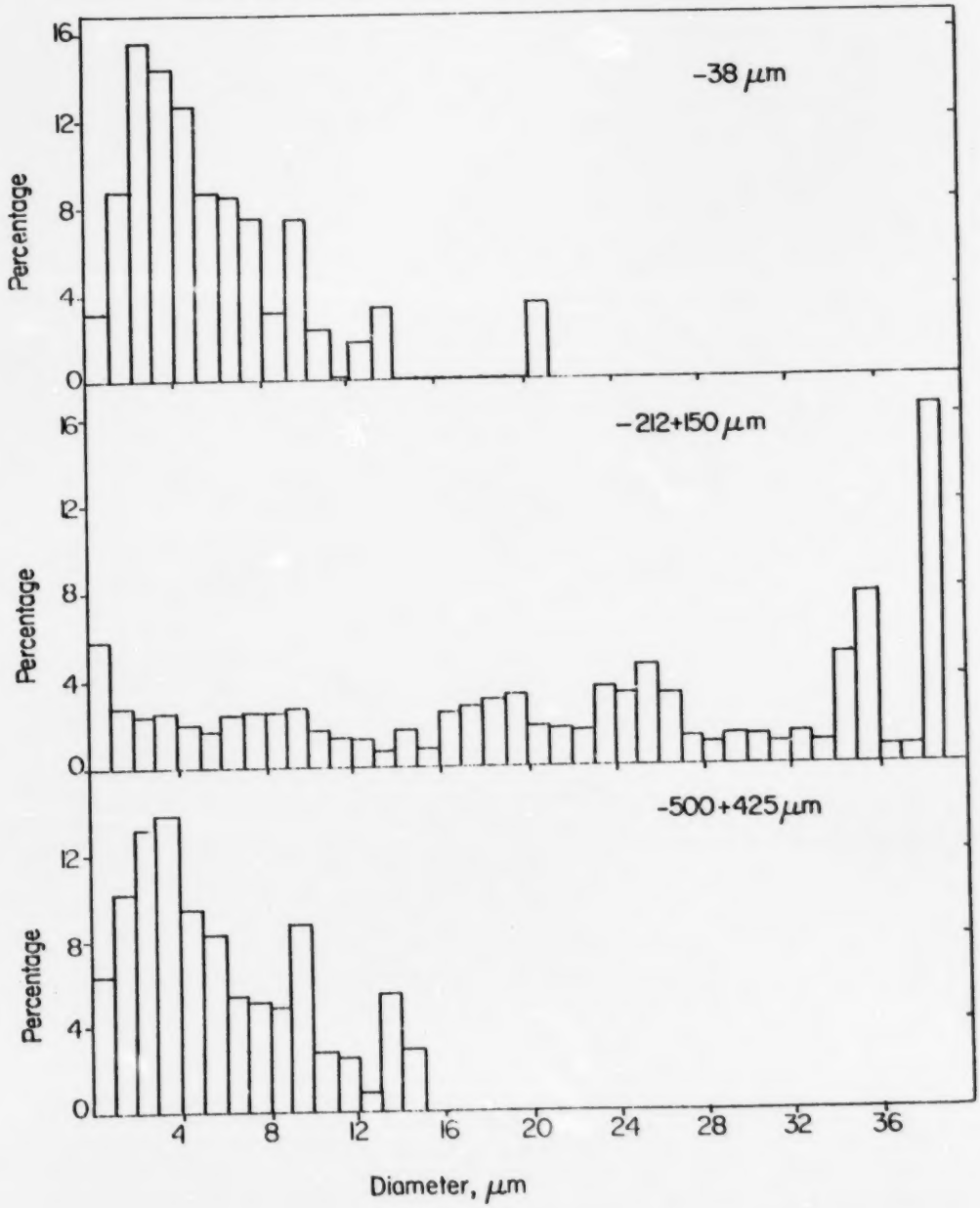


Fig. 5 Pyrite particle size distributions for sample I dry groundbelow 212 μm and screened into various size fractions

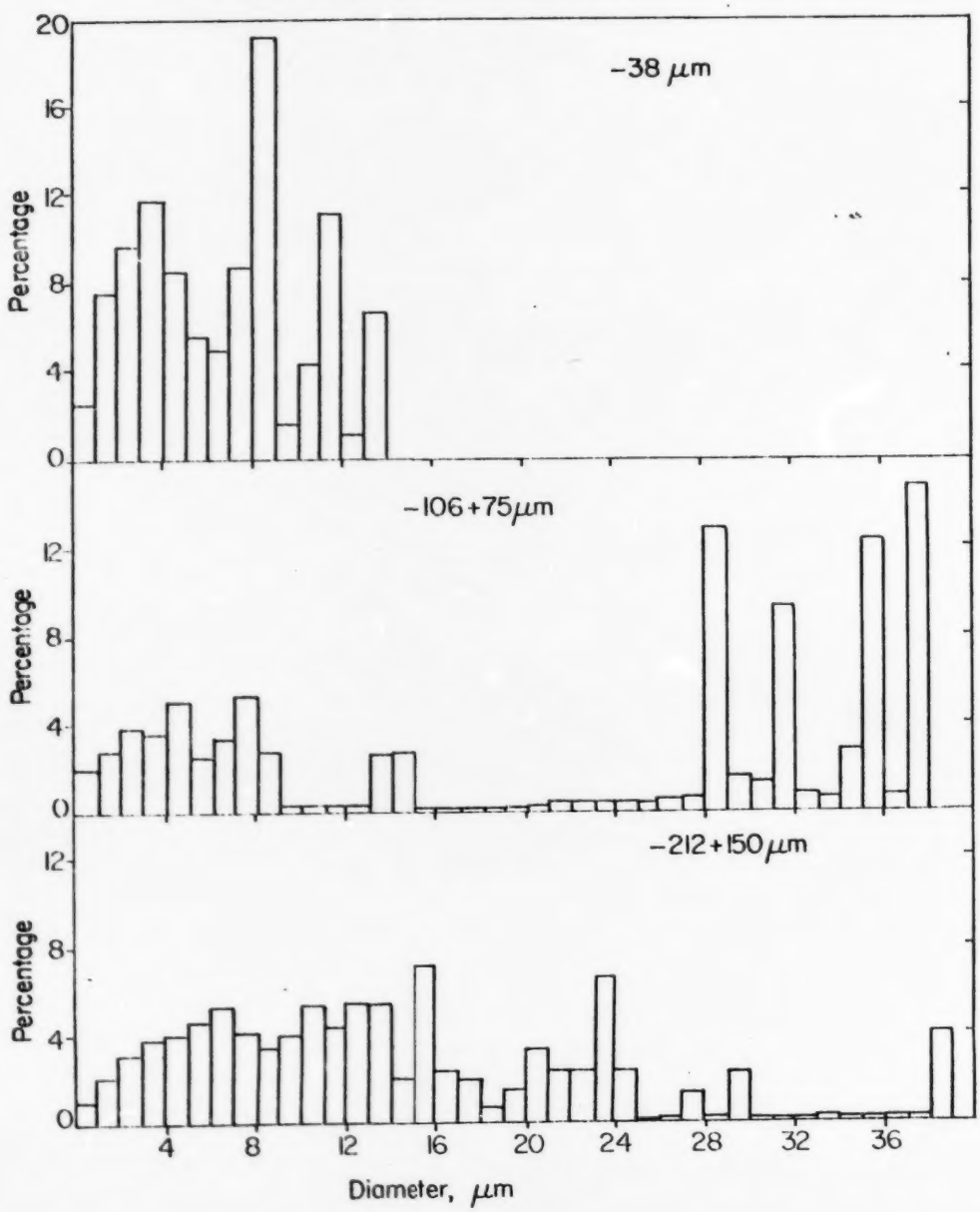


Fig. 6 Pyrite particle size distributions for sample I dry ground below 75 μm and screened into various size fractions

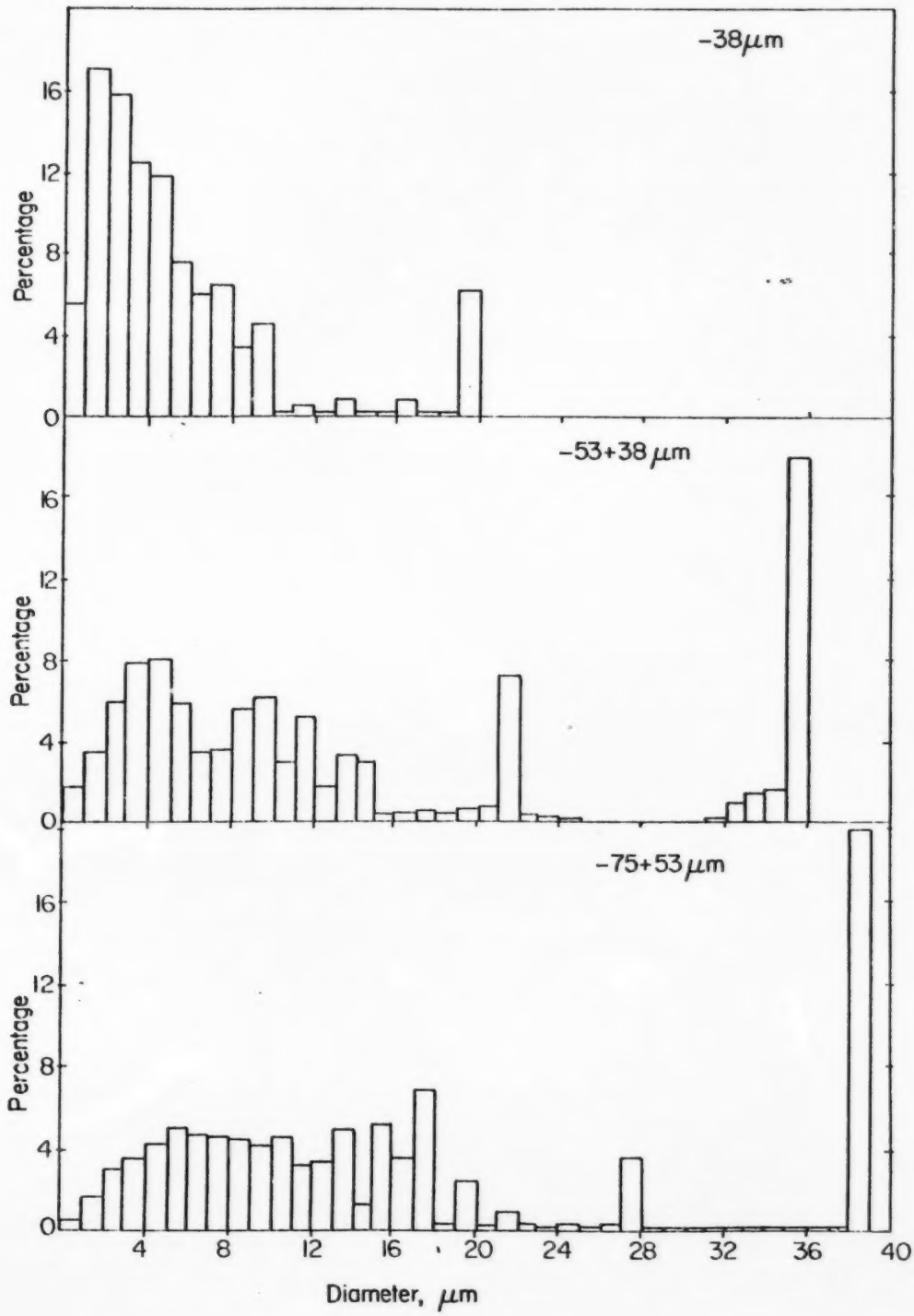


Fig. 7 Pyrite particle size distributions for sample I ground wet below 75 μm and screened into various size fractions

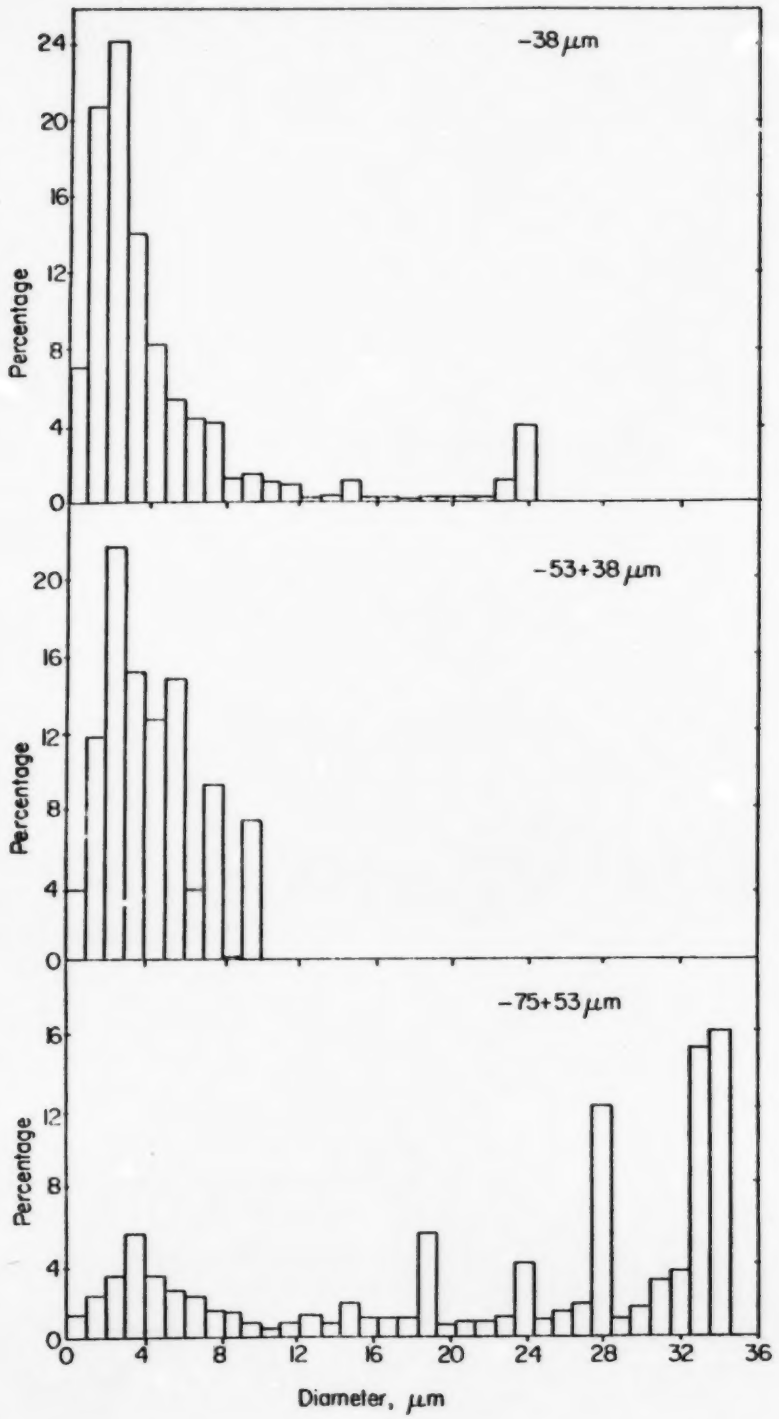


Fig. 8 Variation in pyrite particle size distributions with length of grinding time (15, 21 and 27 minutes) for +38 and -38 fractions

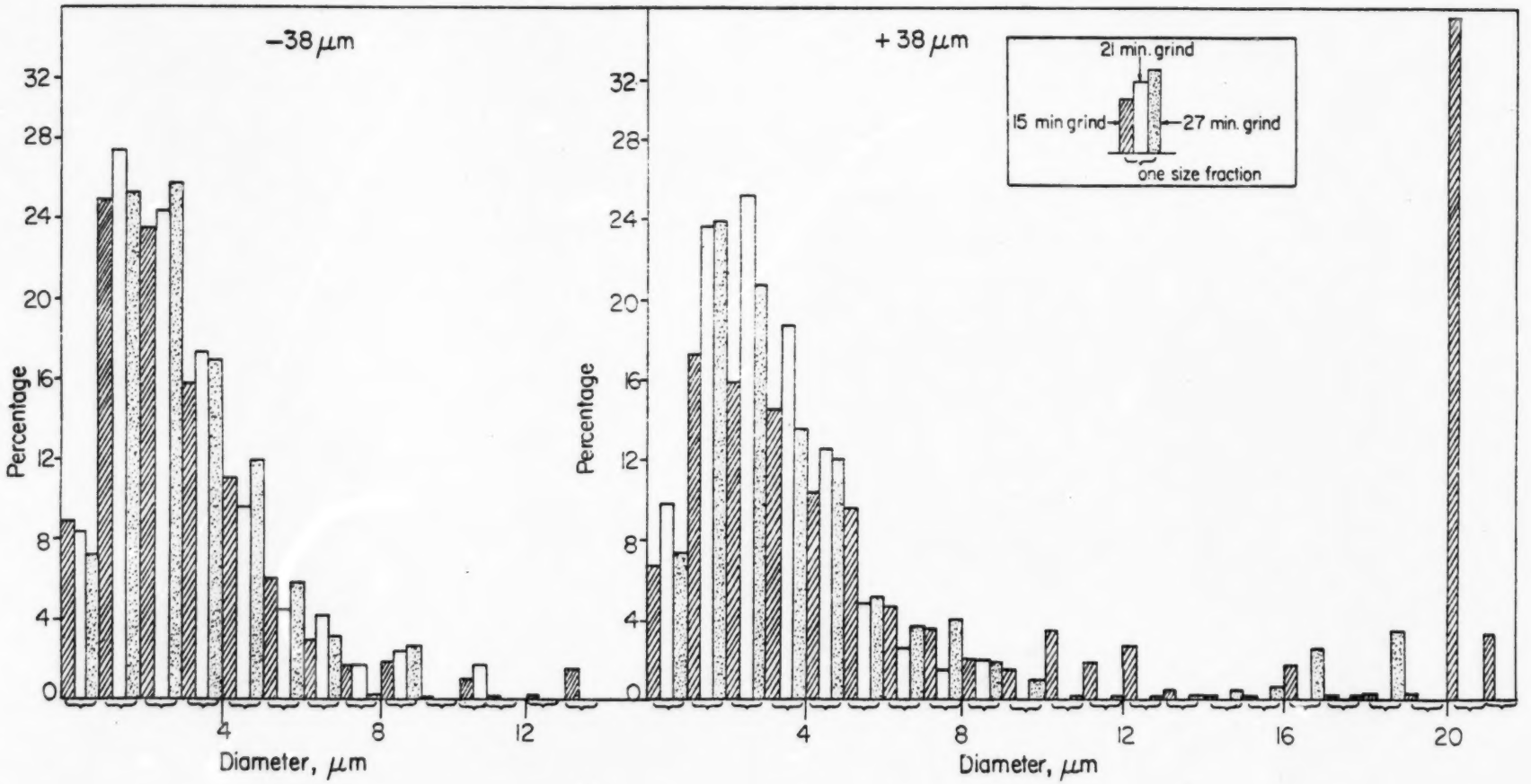
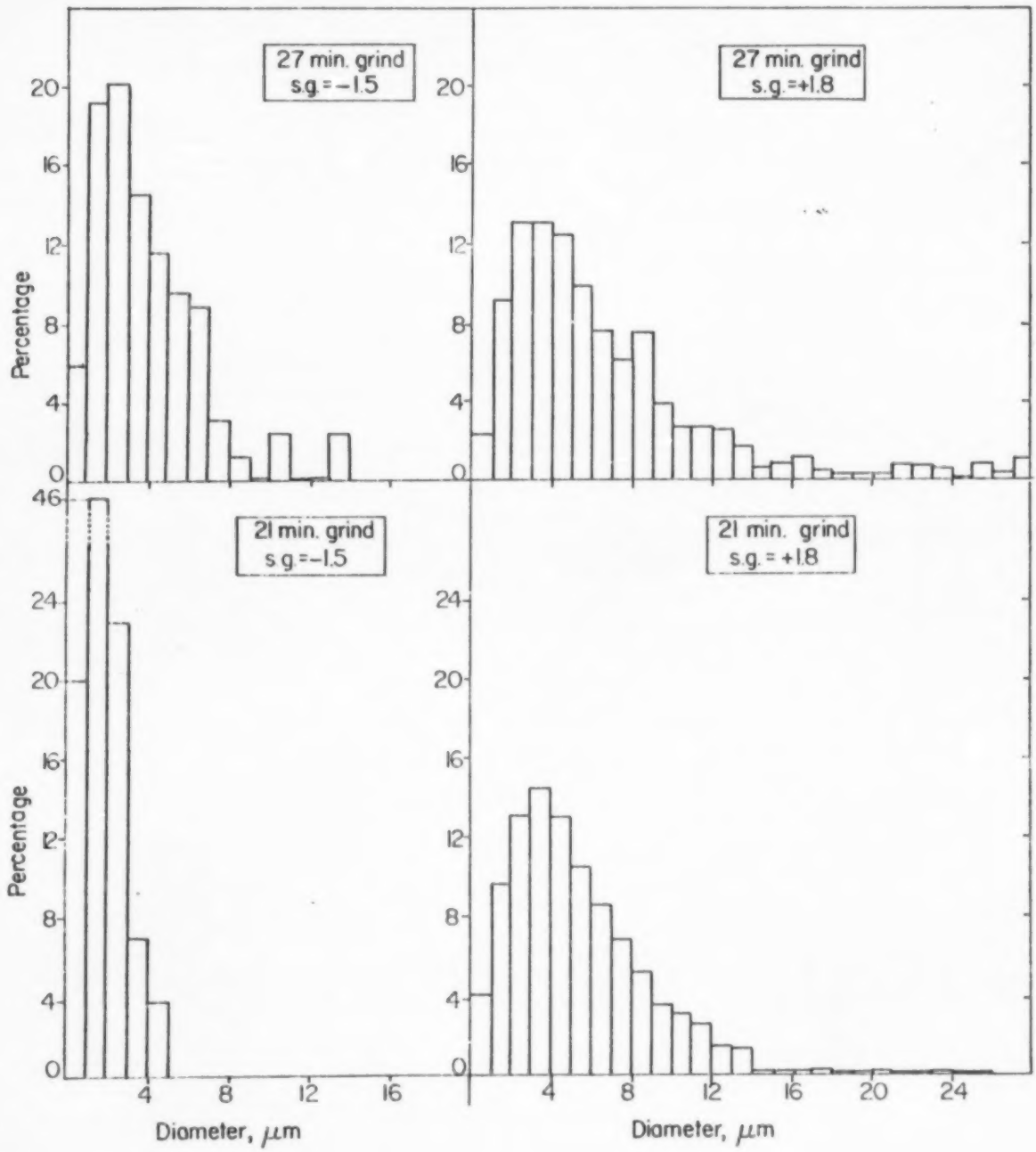


Fig. 9 Pyrite particle size distributions for wet ground fine coal separated in 1.5 and 1.8 heavy liquids (grind times 21 and 27 minutes)



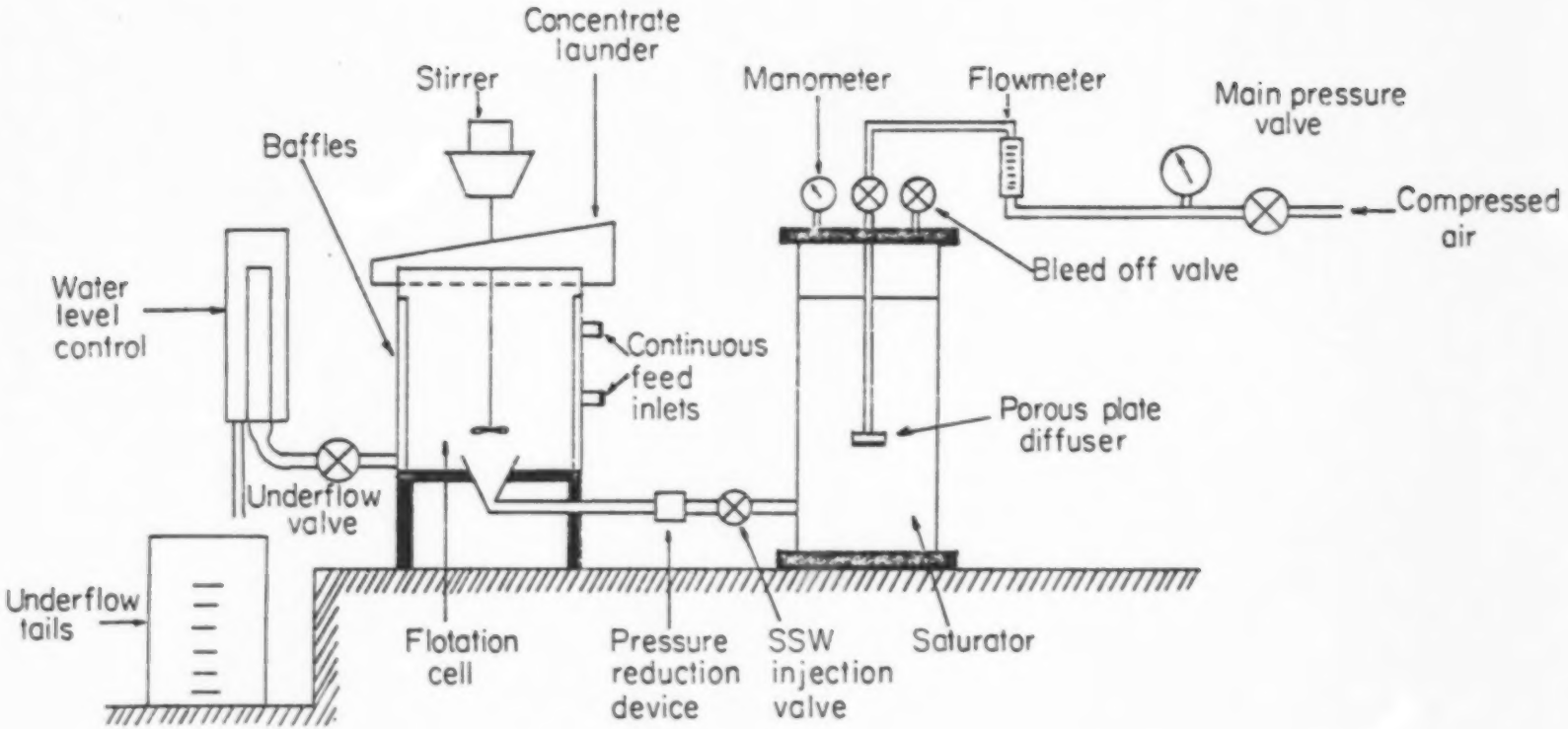


Fig. 10 Batch dissolved air flotation unit

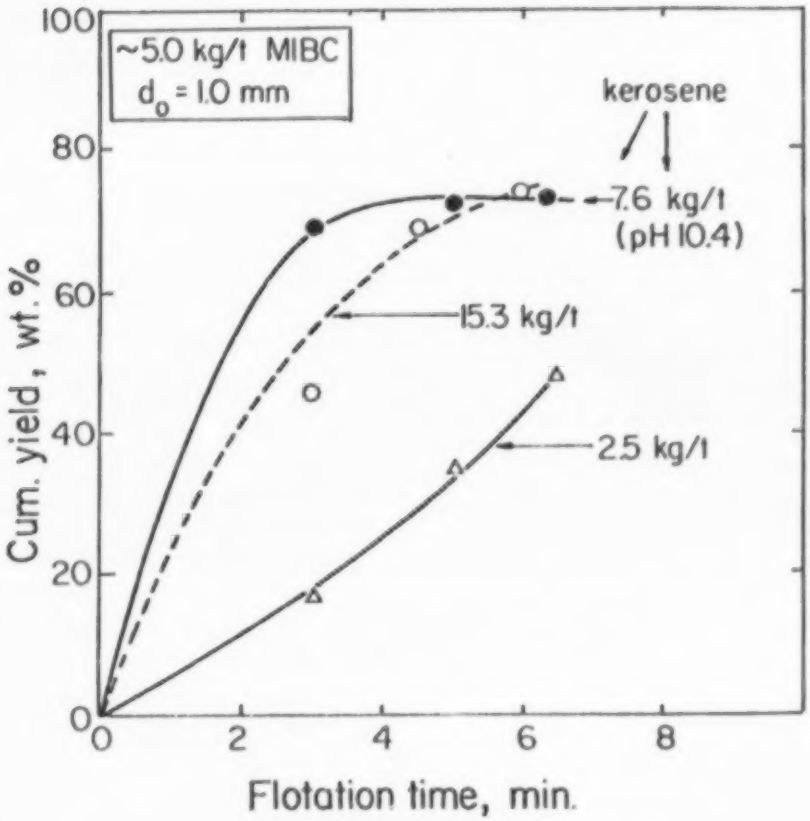


Fig. 11 Kinetics of DAF of Devco coal for various kerosene concentrations (d_o = 1.0 mm)

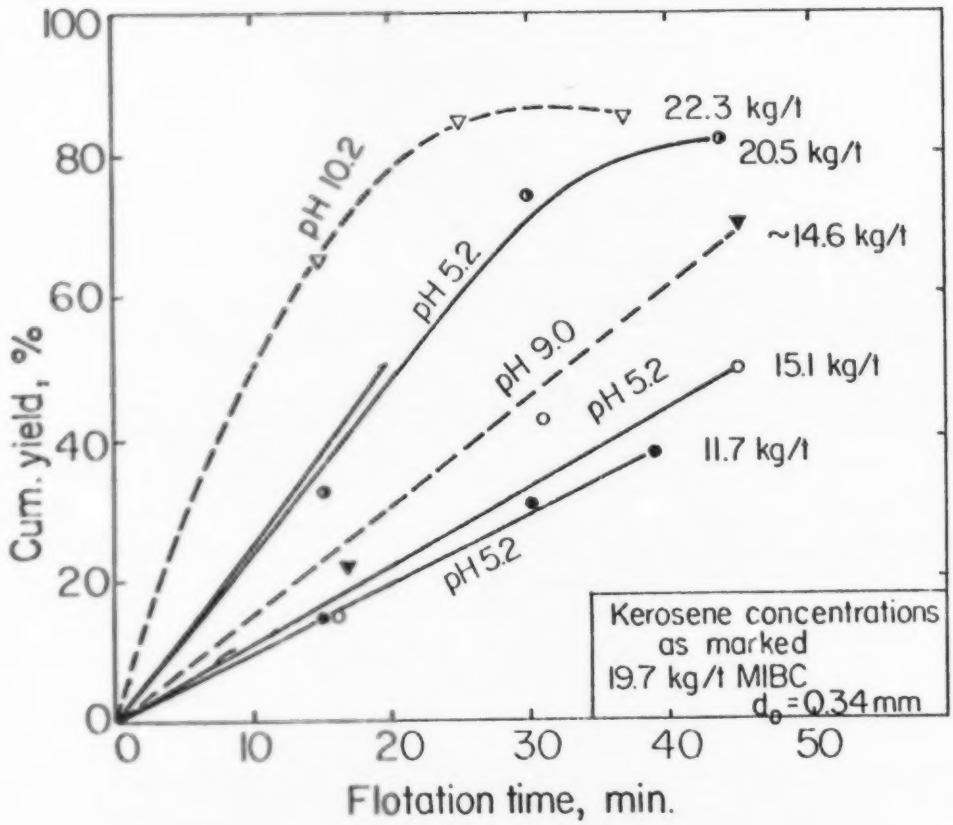


Fig. 12 Kinetics of DAF of Devco coal for various kerosene concentrations (d_o = 0.34 mm)

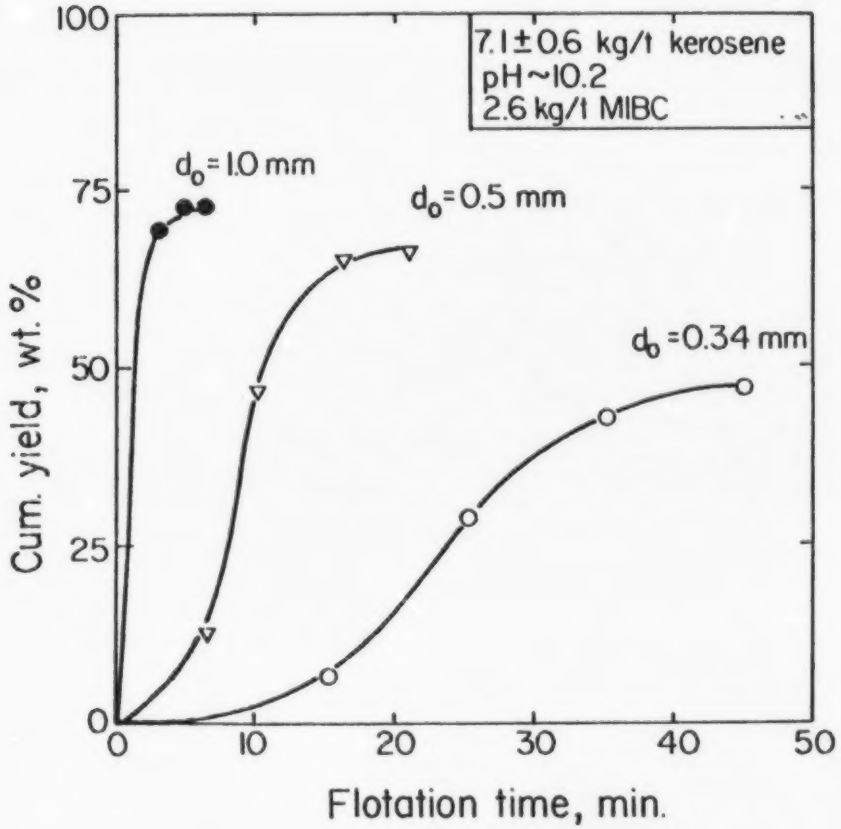


Fig. 13 Recovery as a function of flotation time for various orifice plate diameters

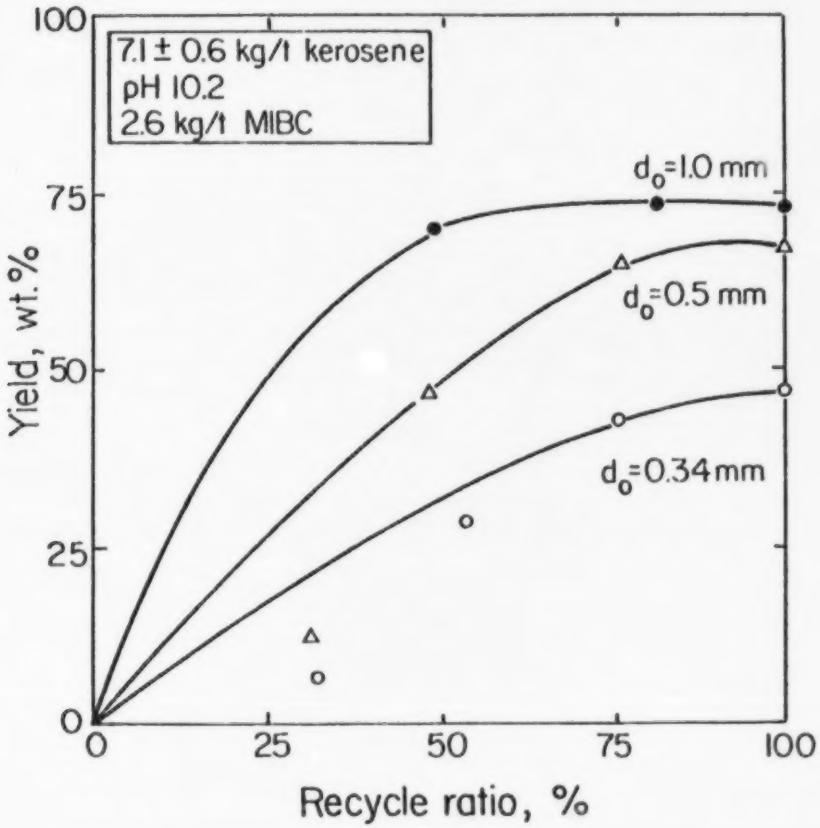


Fig. 14 Effect of recycle ratio on coal recovery for various orifice plate diameters

$$\text{Recycle ratio} = \frac{\text{volume of supersaturated water}}{\text{volume of feed}}$$

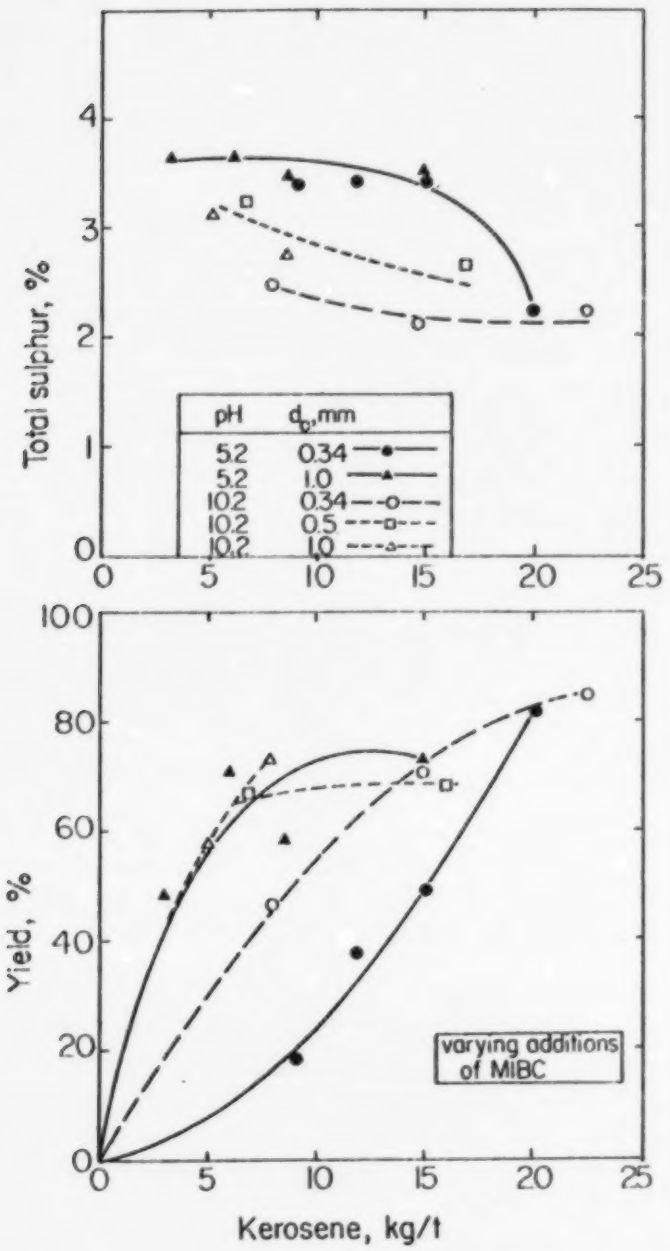


Fig. 15 Effect of kerosene concentration on yield and sulphur content of Devco coal concentrate

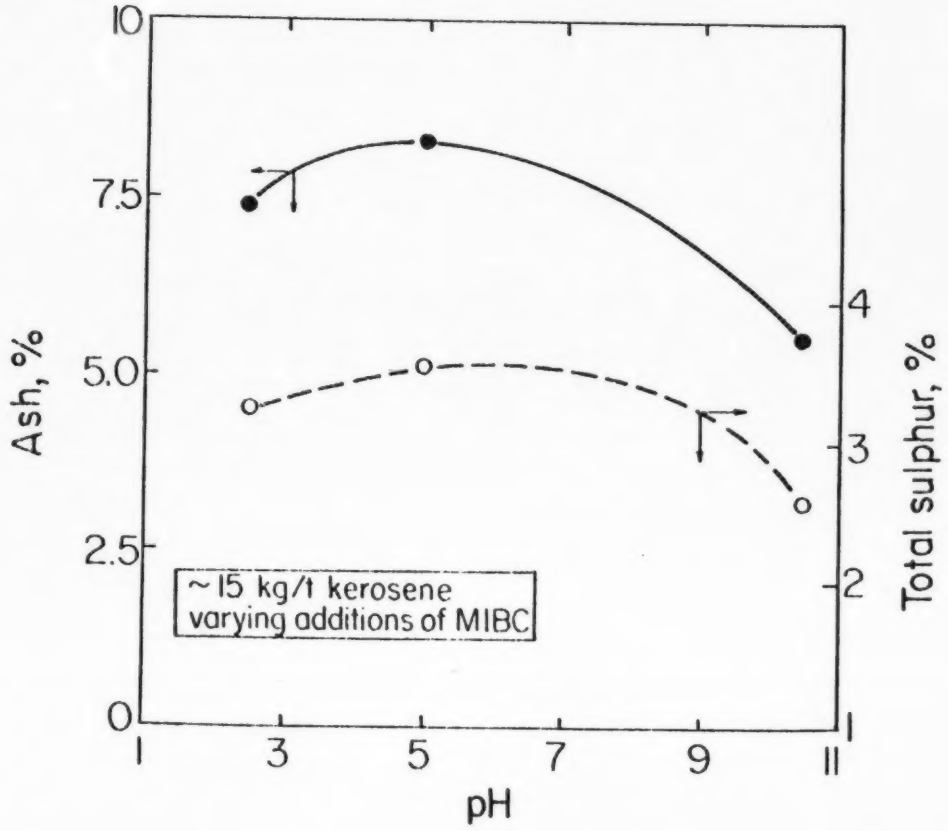


Fig. 16 Effect of pH on DAF of Devco coal

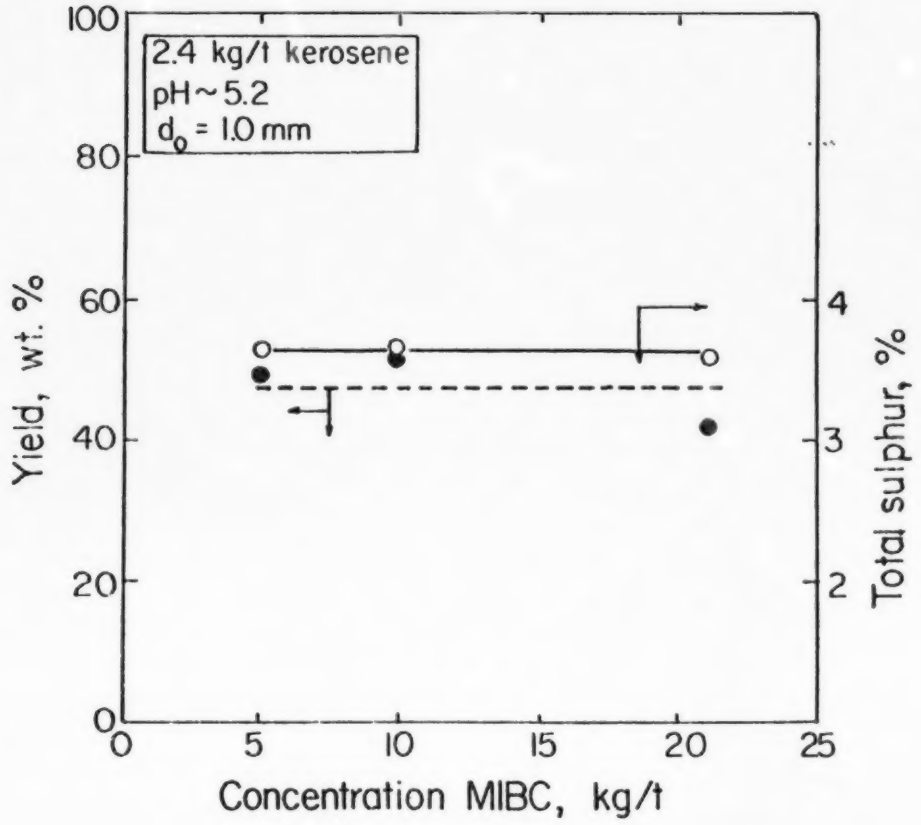


Fig. 17 Effect of MIBC concentration on yield and sulphur content of Devco coal concentrate

Fig. 18a Correlation between water recovery and sulphur content in Devco coal concentrate

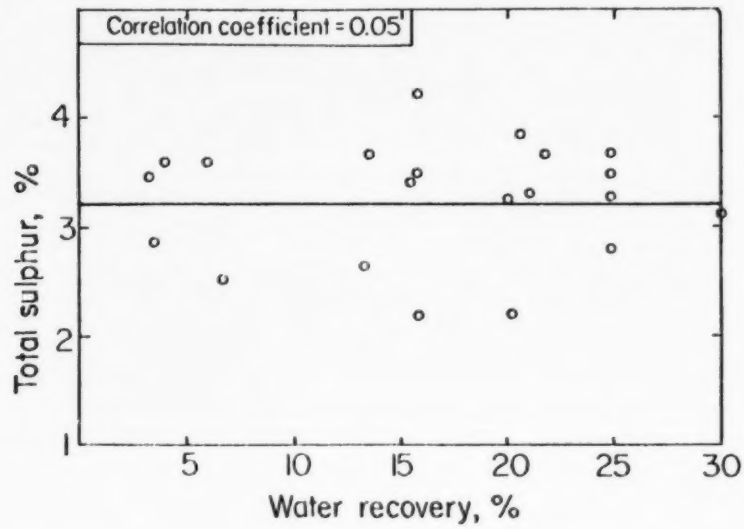
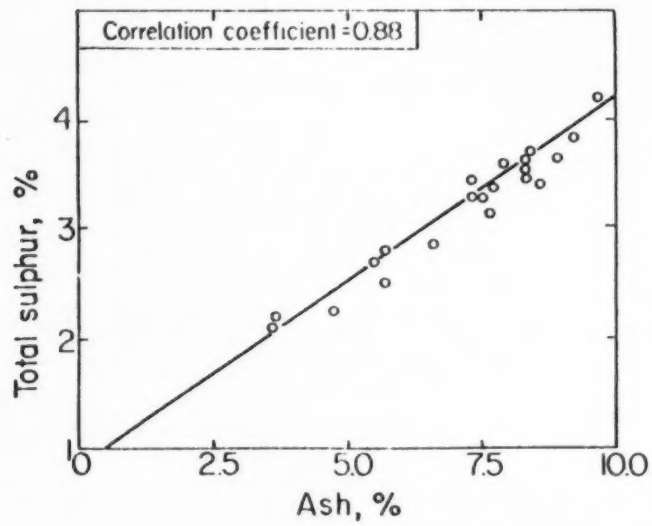


Fig. 18b Correlation between ash and sulphur content in Devco coal concentrate



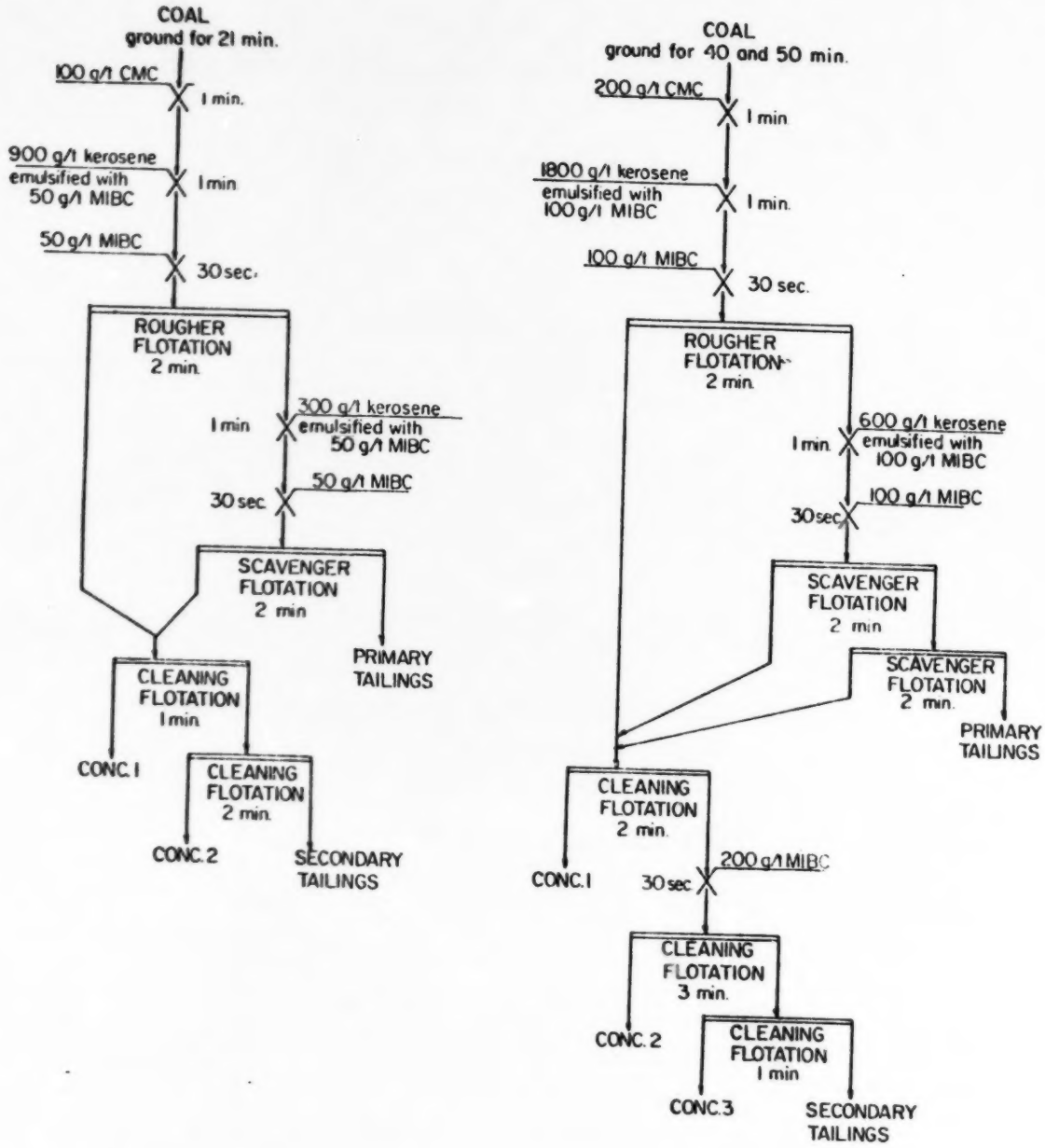


Fig. 19 Schematic illustration of the batch flotation procedures with the use of CMC, kerosene and MIBC

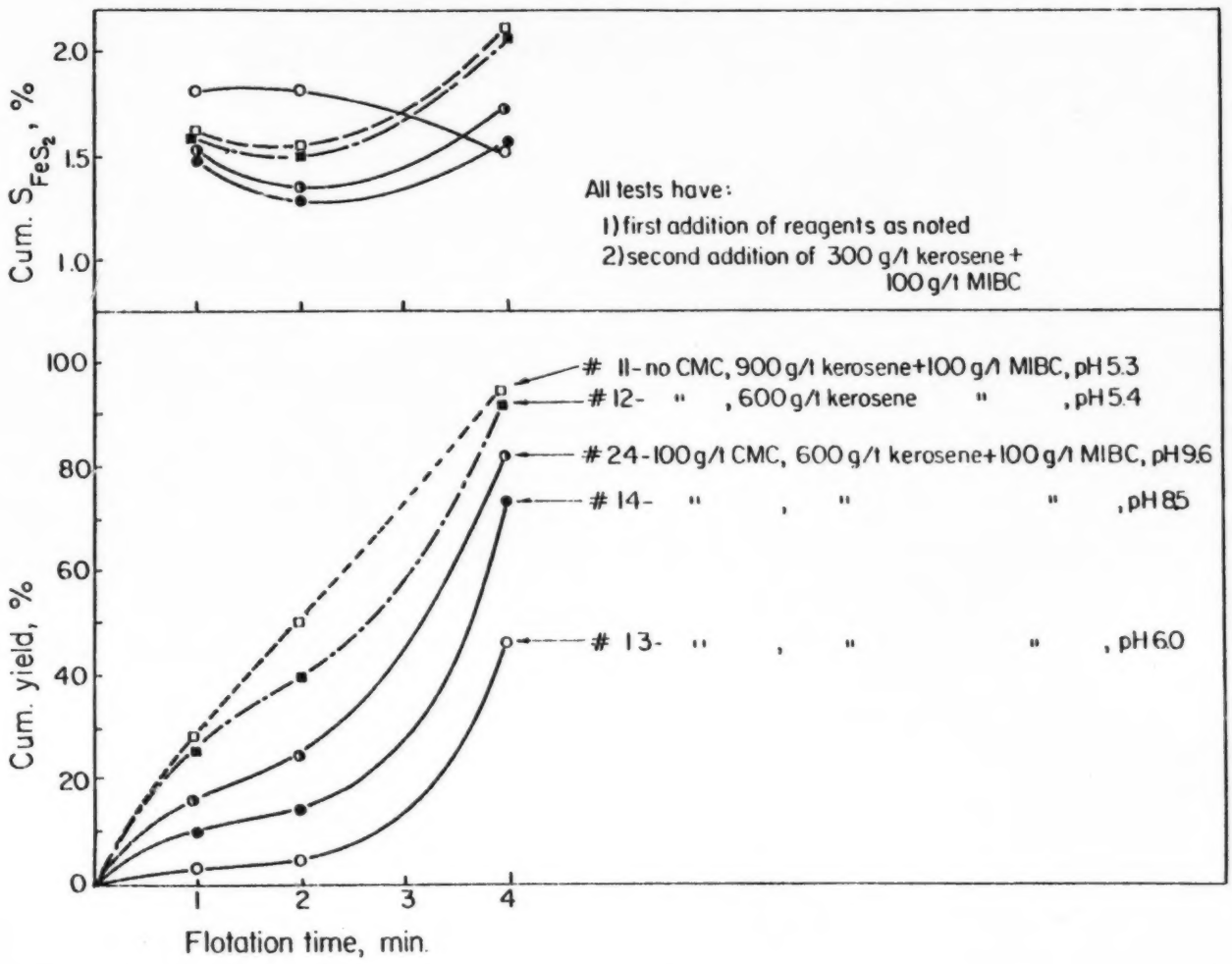

Cum. S_{FeS_2}, %
2.0
1.5
1.0
All tests have:
1) first addition of reagents as noted
2) second addition of 300 g/t kerosene + 100 g/t MIBC
Cum. yield, %
100
80
60
40
20
0
11- no CMC, 900 g/t kerosene+100 g/t MIBC, pH 5.3
12- " , 600 g/t kerosene " , pH 5.4
24- 100 g/t CMC, 600 g/t kerosene+100 g/t MIBC, pH 9.6
14- " , " " , pH 8.5
13- " , " " , pH 6.0
1
2
3
4
Flotation time, min.

Fig. 20 Effect of CMC and pH on the kinetics of flotation of sample 2 coal

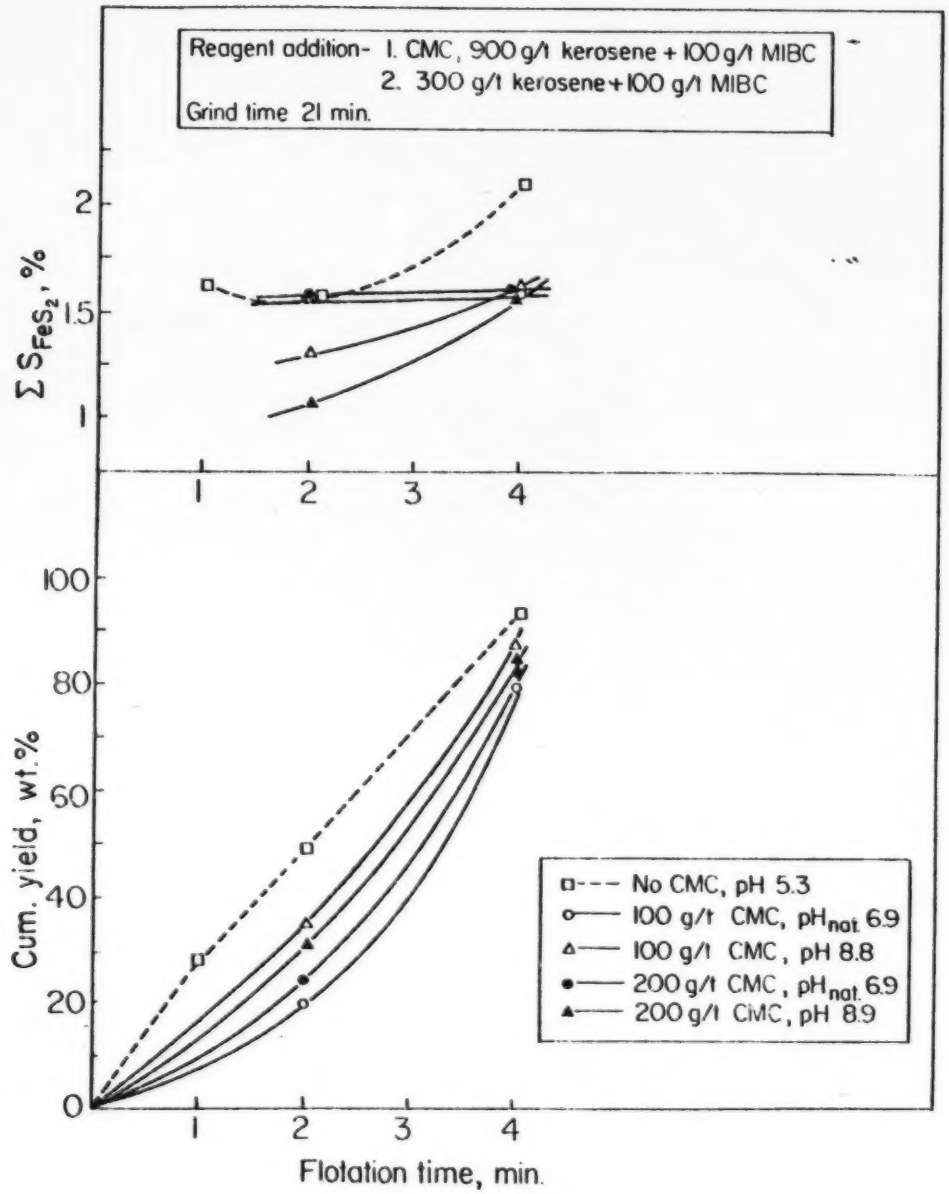


Fig. 21 Effect of CMC and pH on the kinetics of flotation of sample 2 coal

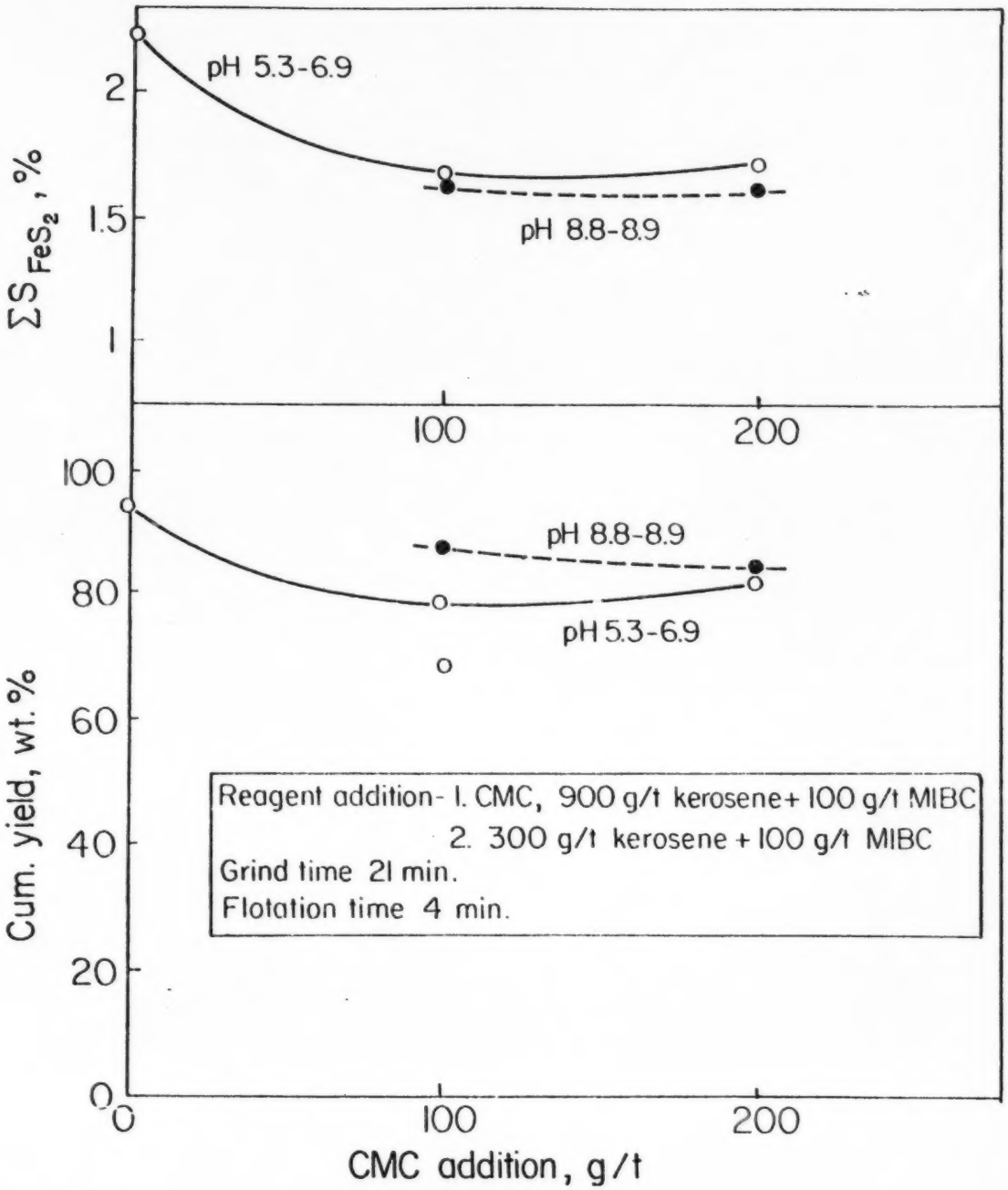


Fig. 22 Effect of pH and CMC on flotation of sample 2 coal

Fig. 23 Humic acid as modifier in froth flotation of sample 2 coal

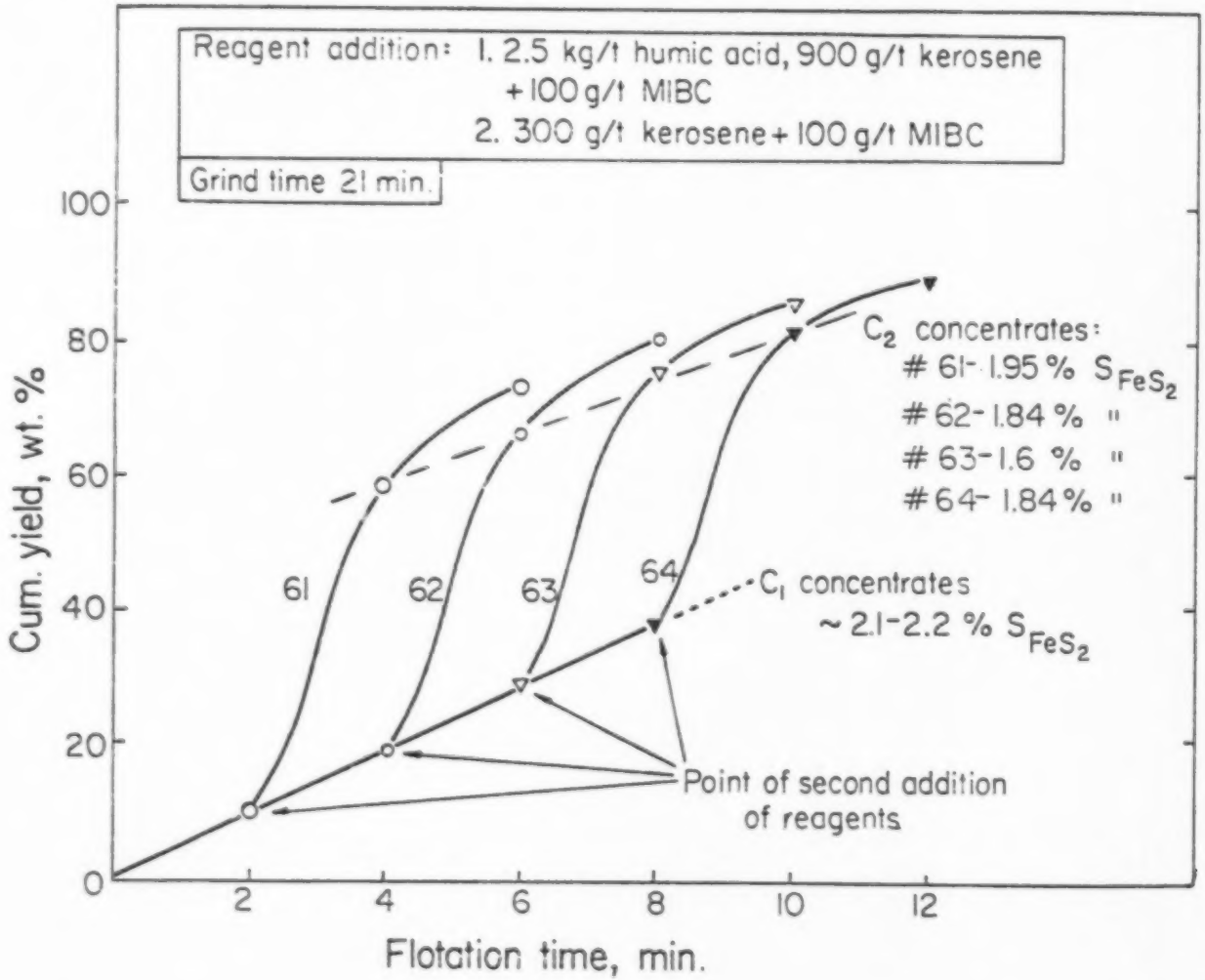
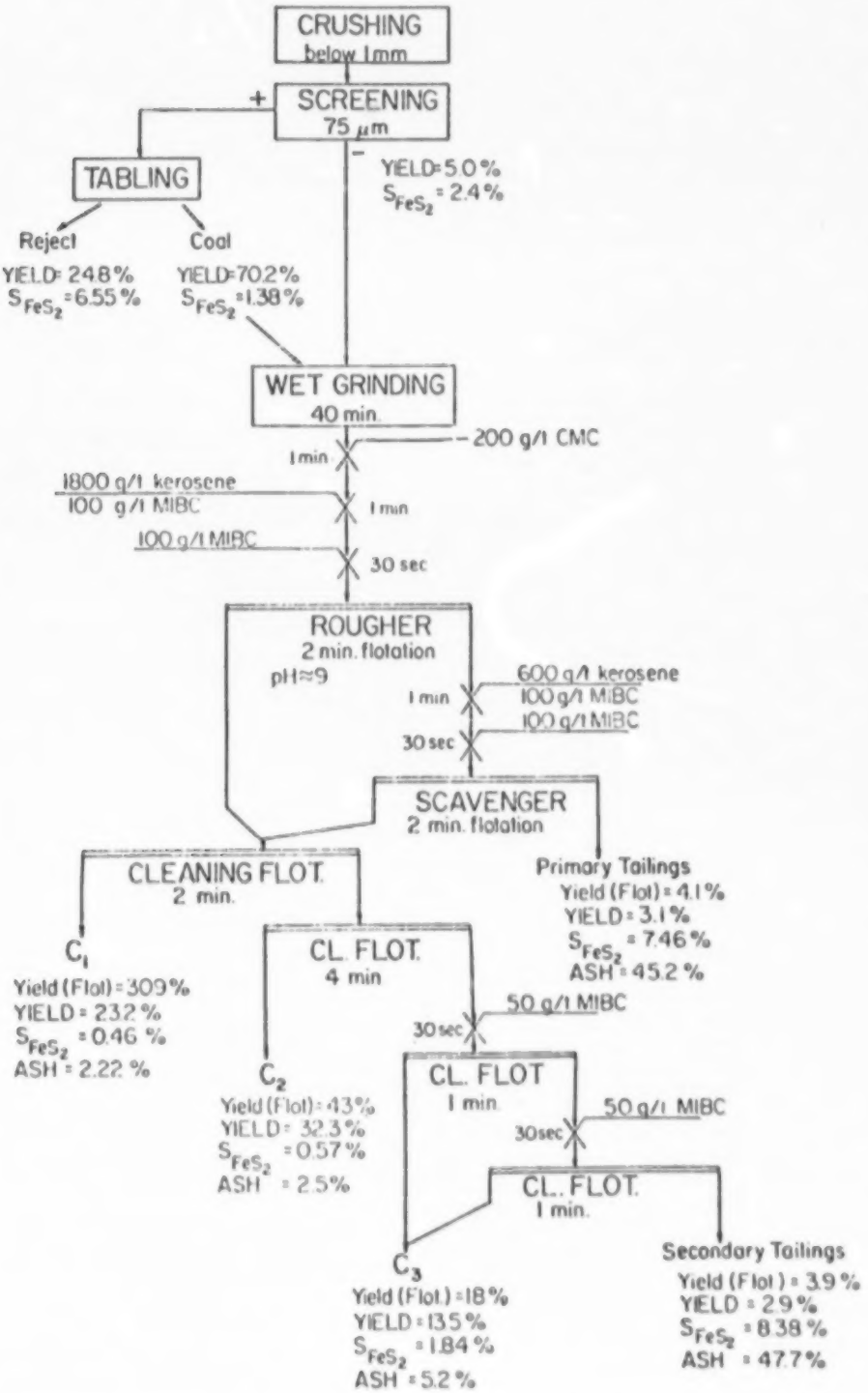

Reagent addition: 1. 2.5 kg/t humic acid, 900 g/t kerosene + 100 g/t MIBC
2. 300 g/t kerosene + 100 g/t MIBC
Grind time 21 min.
Cum. yield, wt. %
Flotation time, min.
C2 concentrates:
61- 1.95 % S FeS2
62- 1.84 % "
63- 1.6 % "
64- 1.84 % "
C1 concentrates
~ 2.1-2.2 % S FeS2
61
62
63
64
Point of second addition of reagents

Fig. 24 Final results and flowsheet developed from testwork



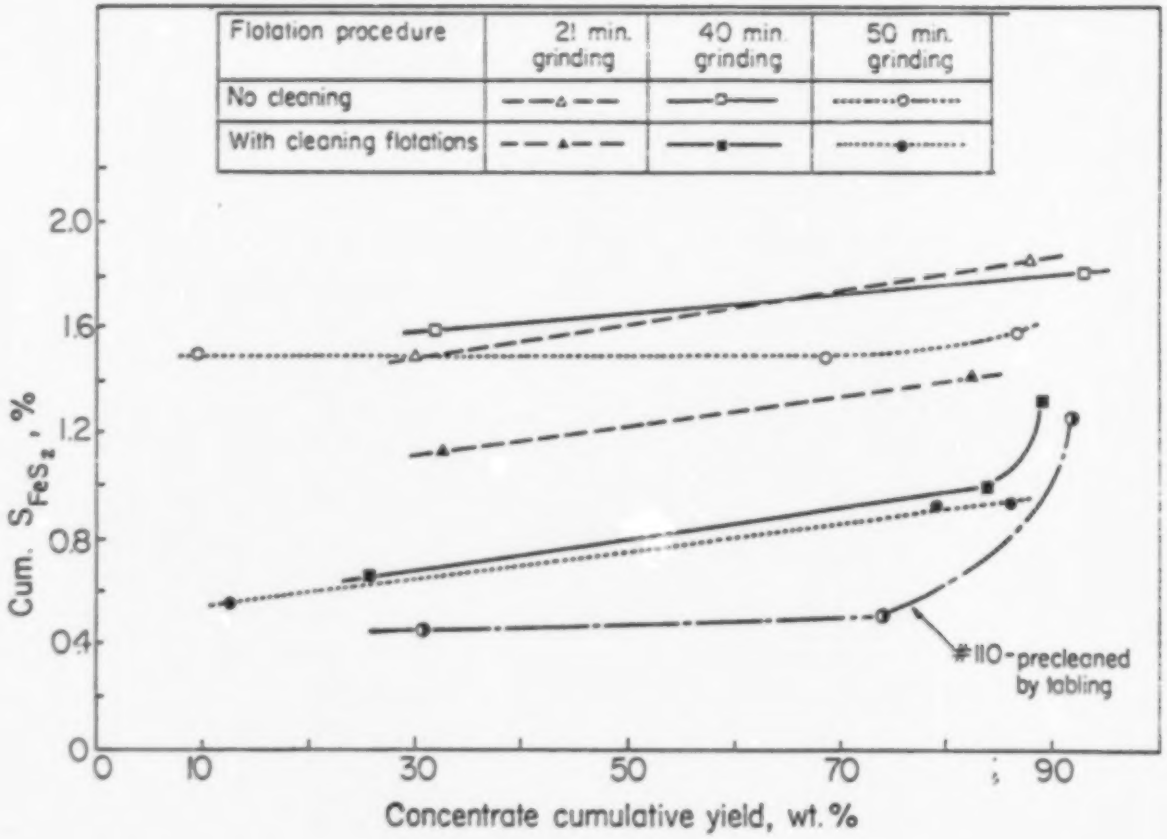


Fig. 25 Effect of grinding time on selectivity of flotation with CMC, kerosene and MIBC

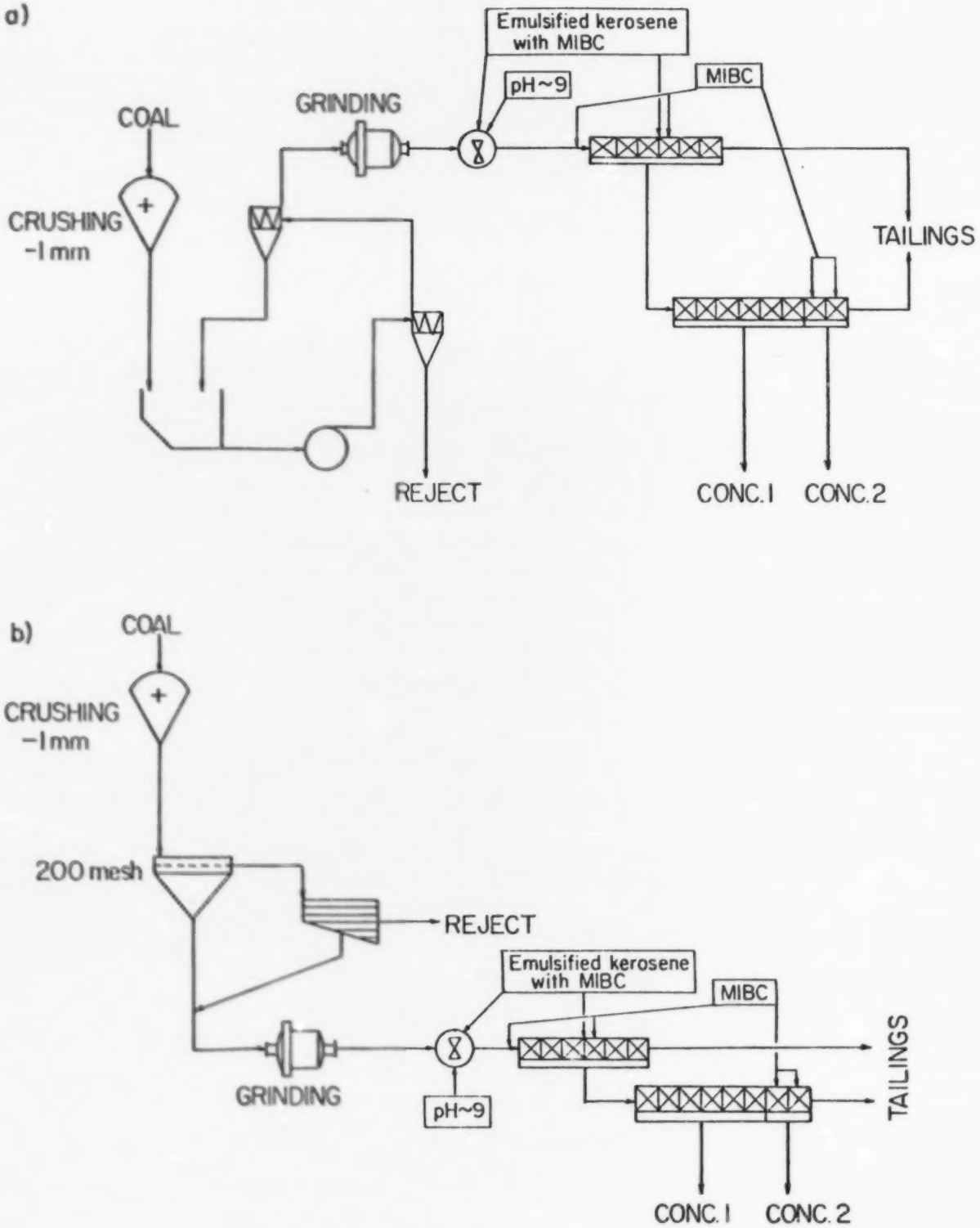


Fig. 26 Suggested flowsheets for pilot plant tests

PLATE

Photographs of Prince Mine coal (No. 2 Sample). All photographs taken with reflected light oil immersion.

1. Raw coal. Photomicrography showing vitrinite (groundmass) with dark liptinite. Very fine pyrite (p) occurs throughout.
2. Raw coal. Photomicrograph showing vitrinite with framboidal pyrite (fp) and fine single pyrite crystals (p).
3. Sample ground wet for 40 minutes. Most of the coarse pyrite has been liberated but fine pyrite particles (p) are still unliberated.
4. Sample C1-32 (21 min. grinding, rougher concentrate: 100 g/t CMC, 900 g/t kerosene + 100 g/t MIBC, 300 g/t kerosene + 100 g/t MIBC, pH 9). Framboidal pyrite (fp) and fine single crystals of pyrite (p) occur throughout the vitrinite.
5. Sample C2-28 (21 min. grinding, second concentrate: 200 g/t CMC, 900 g/t kerosene + 100 g/t MIBC, 300 g/t kerosene + 100 g/t MIBC, pH 8.9). Coarse sub-hedral pyrite (p) crystals within vitrinite particles.
6. Sample C2-28 (as above). Liberated and unliberated framboidal and subhedral pyrite (p).

7,8. Sample C1-28 (as above, first concentrate). Liberated (lp) and non-liberated (np). Because of the method of sample preparation, very fine liberated pyrite is difficult to recognize and thus its abundance is likely underestimated.